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## Kinetics and Mechanism of the First-stage Exothermic Decomposition Reaction for 2,6,8,12-Tetranitro-4,10-bis(2,2,2-trinitroethyl)-2,4,6,8,10,12-hexaazatricyclo[7·3·0·0<sup>3,7</sup>]-dodecane-5,11-dione

HU Rong-zu<sup>1</sup>, YANG De-suo<sup>2</sup>, GAO Sheng-li<sup>1</sup>, ZHAO Hong-an<sup>1</sup>, SHI Qi-zhen<sup>1</sup>

(1. Shaanxi Key Laboratory of Physico-Inorganic Chemistry, Department of Chemistry, Northwest University, Xi'an 710069, China;

2. Department of Chemistry & Department of Chemical Engineering, Baoji College of Arts and Science, Baoji 721007, China)

**Abstract:** The thermal behavior, mechanism and kinetic parameters of the first-stage exothermic decomposition reaction of the title compound in a temperature-programmed mode were investigated by means of DSC, TG-DTG and IR. The reaction mechanism has been proposed. The empirical kinetic model functions in differential forms, the apparent activation energy ( $E_a$ ) and the pre-exponential factor ( $A$ ) of this reaction are  $1/3(1-\alpha)[- \ln(1-\alpha)]^{-2}$ ,  $166.6 \text{ kJ} \cdot \text{mol}^{-1}$  and  $10^{13.29} \text{ s}^{-1}$ , respectively. The critical temperature of thermal explosion of the compound is  $191.16 \text{ }^\circ\text{C}$ . The values of  $\Delta S^\ddagger$ ,  $\Delta H^\ddagger$  and  $\Delta G^\ddagger$  of the reaction are  $50.8 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ ,  $162.9 \text{ kJ} \cdot \text{mol}^{-1}$  and  $139.9 \text{ kJ} \cdot \text{mol}^{-1}$ , respectively.

**Key words:** decomposition; TBHTDD; kinetics; mechanism

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### 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. 2,6,8,12-tetranitro-4,10-bis(2,2,2-trinitroethyl)-2,4,6,8,10,12-hexaazatricyclo[7·3·0·0<sup>3,7</sup>]-dodecane-5,11-dione (1) is a typical cyclourea nitramine. The crystal density is  $1.94 \text{ g} \cdot \text{cm}^{-3}$ . The detonation velocity corresponding to  $\rho = 1.931 \text{ g} \cdot \text{cm}^{-3}$  is about  $9042 \text{ m} \cdot \text{s}^{-1}$ . Therefore, this compound may be used as high explosive. Its thermal behavior has been reported<sup>[1]</sup>. 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.

### 2 Experimental

2,6,8,12-tetranitro-4,10-bis(2,2,2-trinitroethyl)-

2,4,6,8,10,12-hexaazatricyclo[7·3·0·0<sup>3,7</sup>]-dodecane-5,11-dione (1) was prepared in Xi'an Modern Chemistry Research Institute. Its purity was more than 99.5%. The sample was kept in a vacuum desiccator.

TG-DTG curve was obtained by using a Perkin-Elmer Model TGS-2 thermobalance. The heating rate was  $10 \text{ }^\circ\text{C} \cdot \text{min}^{-1}$ . The flow rate of  $\text{N}_2$  gas was  $40 \text{ ml} \cdot \text{min}^{-1}$ . 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  $1 \sim 20 \text{ }^\circ\text{C} \cdot \text{min}^{-1}$ .  $\alpha\text{-Al}_2\text{O}_3$  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  $\text{N}_2$  gas and absorbed in an acetic acid solution of  $\alpha$ -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 compound 1 are shown in Figs. 1 and 2. DSC curve shows two exo-

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**Biography:** HU Rong-zu (1938 - ), male, professor, research fields: thermochemistry and thermal analysis; published over 230 papers.

thermic peaks, while TG curve shows two-stage mass loss without any stable intermediate product formed in which the first stage began at about 120 °C and completed at 212 °C accompanied with 47.1% mass loss. It is in agreement with the theoretical value of the mass loss of 46.3%, corresponding to the loss of the two trinitroethyl groups attached to nitrogen atom on two sides of carbonyl to obtain 2,6,8,12-tetranitro-2,4,6,8,10,12-hexaazatricyclo[7·3·0·0<sup>3,7</sup>]-dodecane-5,11-dione.

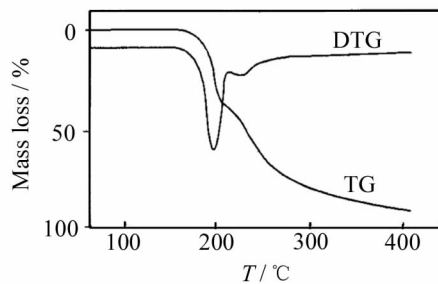


Fig.1 TG-DTG curve for compound 1 at a heating rate of 10 °C · min<sup>-1</sup>

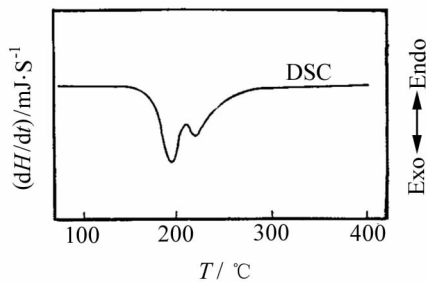
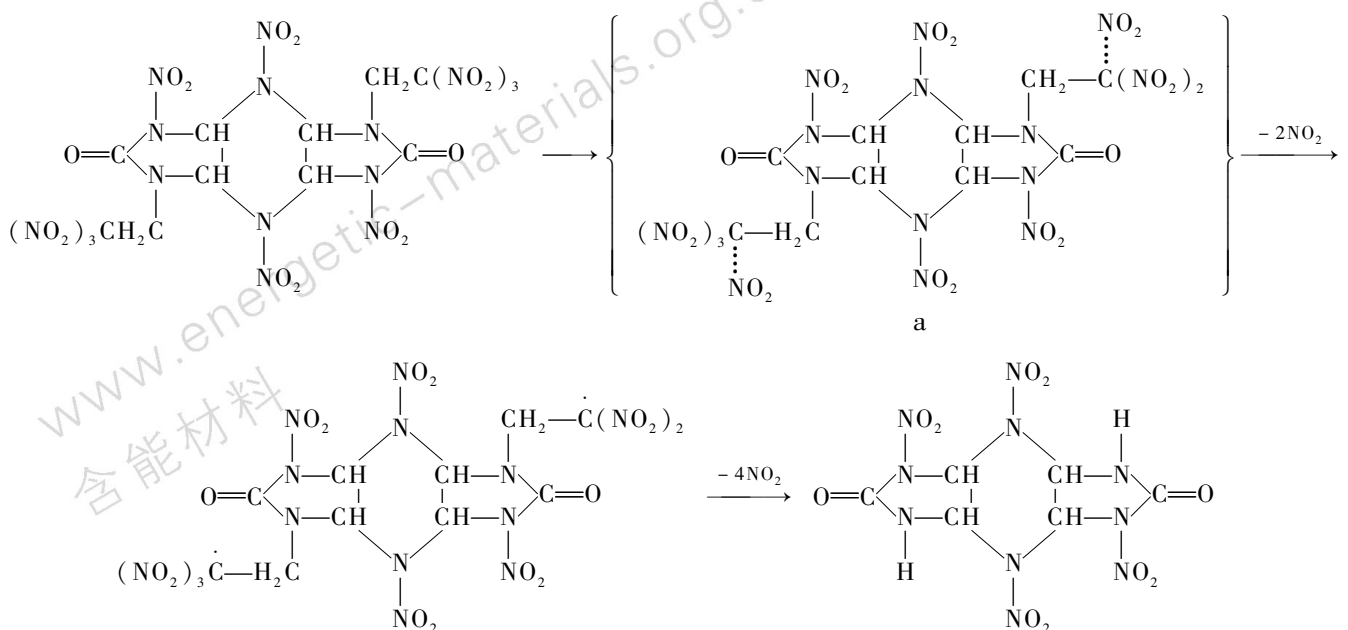


Fig.2 DSC curve for compound 1 at a heating rate of 5 °C · min<sup>-1</sup>

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 decomposition-interruption tests were conducted. By the end of the first-stage, the characteristic absorption peaks for trinitroethyl group of compound 1 disappear at 1 605 and 1 305 cm<sup>-1</sup>. The characteristic absorption peak for the N—H group appears at 3 300 cm<sup>-1</sup> and those of the N—NO<sub>2</sub> group at 1 585 and 1 270 cm<sup>-1</sup> do not disappear. The characteristic absorption peaks of C=O at 1 820 and 1 800 cm<sup>-1</sup> widen. These observations show that the parent ring of compound 1 does indeed exist. 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 follows.



### 3.2 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<sup>[2]</sup> (Kissinger's method) was employed. From the original data in Table 1,  $E_k$  is determined to be 162.9 kJ·mol<sup>-1</sup> and  $A$  10<sup>15.63</sup> s<sup>-1</sup>. The linear correlation coefficient ( $r_k$ ) is 0.998 1. The values of  $E_0$  and  $r_0$  obtained by Ozawa's method<sup>[3]</sup> are 162.4 kJ·mol<sup>-1</sup> and 0.998 3, 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 ( $\beta$ )

$\beta/^\circ\text{C}\cdot\text{min}^{-1}$	0.500	1.053	1.842	5.362	10.07	22.67
$T_p/^\circ\text{C}$	182	188	195	205	213	224

The integral Eq. (1) and differential Eq. (2) 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<sup>[4]</sup>.

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

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

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,  $\alpha$  the conversion degree ( $\alpha = H_t/H_0$ ),  $dH_t/dt$  the exo-

thermic 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  $t$ .

Thirty types of kinetic model function<sup>[5]</sup> 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 ( $r$ ) and standard mean square deviation ( $Q$ ) were obtained by the linear least-squares and iterative methods<sup>[4]</sup>.

**Table 2** Data of compound 1 determined by DSC<sup>a)</sup>

Data point	$T_i/\text{K}$	$\alpha_i$	$(dH_t/dt)_i/\text{mJ}\cdot\text{s}^{-1}$
1	436.2	0.0283	2.6778
2	448.2	0.0468	3.1798
3	458.2	0.0682	4.0166
4	470.2	0.0916	5.0208
5	483.2	0.1345	8.3680
6	491.2	0.1667	13.724
7	497.2	0.2164	19.916

Note: a)  $T_0 = 400.2$  K;  $H_0 = 5151.3$  mJ;  $\beta = 0.3333$  °C·s<sup>-1</sup>

The probable kinetic model functions of the integral and differential methods selected by the logical choice method<sup>[4]</sup> and satisfying ordinary range of the thermal decomposition kinetic parameters for energetic materials ( $E = 80 \sim 250$  kJ·mol<sup>-1</sup>,  $\log A = 7 \sim 30$  s<sup>-1</sup>) are  $f(\alpha) = (1 - \alpha)[- \ln(1 - \alpha)]^{-2}$  and  $G(\alpha) = [- \ln(1 - \alpha)]^3$ . The corresponding kinetic parameters are summarized in Table 3.

**Table 3** Kinetic parameters obtained by the data in Table 2

Equation	$f(\alpha)$	$E/\text{kJ}\cdot\text{mol}^{-1}$	$\log(A/\text{s}^{-1})$	$r$	$Q$
(1)	$\frac{1}{3}(1 - \alpha)[- \ln(1 - \alpha)]^{-2}$	152.1	11.58	0.9970	0.1327
(2)	$\frac{1}{3}(1 - \alpha)[- \ln(1 - \alpha)]^{-2}$	166.6	13.29	0.9901	0.5289

The values of  $E_a$  and  $A$  obtained by Eqs. (1) and (2) 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<sub>2</sub> 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. (3) taken from Ref. [6] is 180.12 °C.

$$T_{pi} = T_{p0} + b\beta_i + c\beta_i^2 + d\beta_i^3, i = 1, 2, 3, 4, 5, 6 \quad (3)$$

where  $b$ ,  $c$  and  $d$  are coefficients.

The critical temperature of thermal explosion ( $T_b$ )

obtained from Eq. (4) taken from Ref. [6] is 191.16 °C.

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

where  $R$  is the gas constant ( $8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ ),  $E_0$  is the value of  $E$  obtained by Ozawa's method.

The entropy of activation ( $\Delta S^\ddagger$ ), enthalpy of activation ( $\Delta H^\ddagger$ ) and free energy of activation ( $\Delta G^\ddagger$ ) corresponding to  $T = T_{po}$ ,  $E = E_k$  and  $A = A_k$  obtained by Eqs. (5), (6) and (7) are  $50.8 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ ,  $162.9 \text{ kJ} \cdot \text{mol}^{-1}$  and  $139.9 \text{ kJ} \cdot \text{mol}^{-1}$ , respectively.

$$A = \frac{k_B T}{h} e^{\Delta S^\ddagger / R} \quad (5)$$

$$A \exp\left(-\frac{E}{RT}\right) = \frac{k_B T}{h} \exp\left(\frac{\Delta S^\ddagger}{R}\right) \exp\left(-\frac{\Delta H^\ddagger}{RT}\right) \quad (6)$$

$$\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger \quad (7)$$

where,  $k_B$  is the Boltzmann constant ( $1.3807 \times 10^{-23} \text{ J} \cdot \text{K}^{-1}$ ) and  $h$  the Planck constant ( $6.626 \times 10^{-34} \text{ J} \cdot \text{s}$ ).

#### 4 Conclusions

The mechanism of the exothermic first-stage decomposition reaction for compound 1 could be expressed as scheme 1. The empirical kinetic model function in differential form, apparent activation energy and pre-exponential constant of this reaction are  $(1 - \alpha[-\ln(1 - \alpha)]^{-2})$ ,

$166.6 \text{ kJ} \cdot \text{mol}^{-1}$  and  $1.01329 \text{ s}^{-1}$ , respectively. The critical temperature of thermal explosion of the compound is 191.16 °C. The values of ( $\Delta S^\ddagger$ ), ( $\Delta H^\ddagger$ ) and ( $\Delta G^\ddagger$ ) of the reaction at  $T_{po}$  are  $50.8 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ ,  $162.9 \text{ kJ} \cdot \text{mol}^{-1}$  and  $139.9 \text{ kJ} \cdot \text{mol}^{-1}$ , respectively.

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## 2,6,8,12-四硝基-4,10-二(2,2,2-三硝基乙基)-2,4,6,8,10,12-六氮杂三环[7·3·0·0<sup>3,7</sup>]十二烷二酮-5,11 放热第一阶段分解反应的动力学和机理

胡荣祖<sup>1</sup>, 杨得锁<sup>2</sup>, 高胜利<sup>1</sup>, 赵宏安<sup>1</sup>, 史启祯<sup>1</sup>

(1. 陕西省物理无机化学重点实验室/西北大学化学系, 陕西 西安 710069;

2. 宝鸡文理学院化学化工系, 陕西 宝鸡 721007)

**摘要:** 在程序升温条件下, 用 DSC、TG-DTG 和 IR, 研究了标题化合物的热行为和放热第一阶段分解反应的动力学和机理。提出了反应机理。该反应的微分形式的动力学模式函数、表观活化能 ( $E_a$ ) 和指前因子 ( $A$ ) 分别为  $1/3(1 - \alpha)[- \ln(1 - \alpha)]^{-2}$ ,  $166.6 \text{ kJ} \cdot \text{mol}^{-1}$  和  $10^{13.29} \text{ s}^{-1}$ 。标题化合物的热爆炸临界温度为 191.16 °C。该反应的  $\Delta S^\ddagger$ 、 $\Delta H^\ddagger$  和  $\Delta G^\ddagger$  分别为  $50.8 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ 、 $162.9 \text{ kJ} \cdot \text{mol}^{-1}$  和  $139.9 \text{ kJ} \cdot \text{mol}^{-1}$ 。

**关键词:** 分解; TBHTDD; 动力学; 机理

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