

## Kinetics and Mechanism of the Exothermic First-stage Decomposition Reaction of Dinitroglucuril

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Under linear temperature increase condition, the thermal behavior, mechanism and kinetic parameters of the exothermic decomposition reaction of the title compound have been studied by means of DSC and IR. The initial stage of the mechanism was proposed. The empirical kinetic model function in differential form, apparent activation energy and pre-exponential constant of the exothermic decomposition reaction are  $\alpha^{0.526}$ , 207.0 kJ·mol<sup>-1</sup> and 10<sup>18.49</sup> s<sup>-1</sup>, respectively. The critical temperature of the thermal explosion of the compound is 252.87 °C. The values of  $\Delta S^\ddagger$ ,  $\Delta H^\ddagger$  and  $\Delta G^\ddagger$  of the reaction are 128.4 J·mol<sup>-1</sup>·K<sup>-1</sup>, 218.9 kJ·mol<sup>-1</sup> and 152.7 kJ·mol<sup>-1</sup>, respectively.

**Keywords** decomposition, dinitroglucuril, DSC, kinetics, mechanism

### Introduction

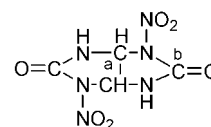
Dinitroglucuril (DINGU) is a typical cyclourea nitramine. Its crystal density is 1.94 g·cm<sup>-3</sup>. The detonation velocity corresponding to  $\rho = 1.94$  g·cm<sup>-3</sup> is about 8450 m·s<sup>-1</sup>. Its sensitivity to impact is better than that of cyclotrimethylenetrinitramine. It has the potential for possible use as high explosive from the point of view of the above-mentioned high performance. Its preparation,<sup>1-4</sup> properties<sup>1-4</sup> and hydrolytic behavior<sup>4</sup> have been reported. In the present paper, we report its kinetic parameters and mechanism of the exothermic decomposition reaction studied with DSC 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.

### Experimental

#### Materials

Dinitroglucuril was prepared according to the reported method.<sup>1</sup> The compound (Scheme 1) was purified by recrystallization from nitric acid for analysis. <sup>1</sup>H NMR (acetone, TMS, 90 MHz)  $\delta$ : 6.08 (CH), 9.87 (NH); <sup>13</sup>C NMR  $\delta$ : 64.25 (C<sub>a</sub>), 149.36 (C<sub>b</sub>); IR (KBr)  $\nu$ : 3370 (NH), 2990 (CH), 1800, 1840 (>C=O), 1590, 1310 (NNO<sub>2</sub>) cm<sup>-1</sup>; MS (70 eV)  $m/z$ : 232 (M<sup>+</sup>), 133, 101, 75, 57, 46, 44, 30. Anal. calcd for C<sub>4</sub>H<sub>4</sub>N<sub>6</sub>O<sub>6</sub>: C 20.70, H 1.74, N 36.21; found C 20.54, H 1.67, N 36.40.

#### Scheme 1



Sample was kept in a vacuum desiccator before use

#### Experimental equipment and conditions

DSC experiments were carried out with a model CDR-1 thermal analyzer made in 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<sup>-1</sup>. DSC curves were obtained with a cell of aluminium (diameter 5 mm×3 mm), whose side is rolled up.  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> was used as reference material in the DSC measurements. The sample mass was about 0.7 mg. The calorimetric sensitivities were  $\pm 41.84$  mJ·s<sup>-1</sup>. The heating rate was calculated according to the actual rising rate of temperature from 50 °C to the temperature at the end of the reaction. The precision of temperature was 0.25 °C. The temperature and heat were calibrated using pure indium and tin powders. DSC curves obtained under the same conditions overlapped with each other, indicating that the reproducibility of tests was satisfactory. The infrared spectra of solid intermediate products were recorded using a Perkin Elmer Model 180 IR spectrophotometer.

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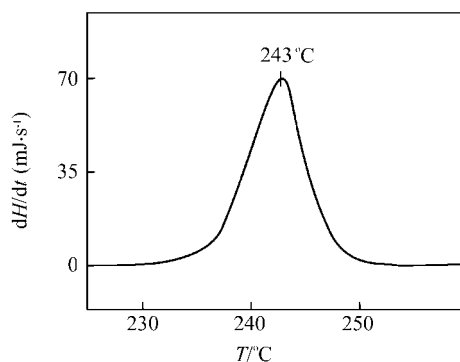
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## Results and discussion

### Thermal behavior and decomposition mechanism

Typical DSC curve for the title compound is shown in Figure 1. It shows only one exothermic peak. In order to understand the initial stage of decomposition process of the title compound, decomposition-interruption tests were conducted with DSC experiments at a heating rate of  $2\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ . Thermal degradation of the title compound was performed by heating the sample to a certain temperature in the first-stage decomposition followed by cooling it down to the room temperature.

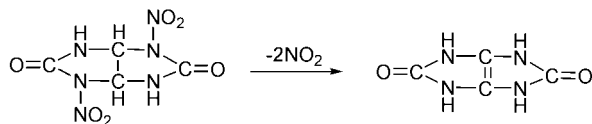


**Figure 1** DSC curve for the title compound at a heating rate of  $2\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ .

The infrared analyses of the title compound before and after thermal decomposition were conducted. The characteristic absorption peaks for the N-NO<sub>2</sub> group of the title compound at about 243 °C disappeared at 1590 and 1310  $\text{cm}^{-1}$ . The characteristic absorption peak for the C-C group appeared at 1600  $\text{cm}^{-1}$  and those of the N-H group at 3320 and 3080  $\text{cm}^{-1}$  and >C=O group at 1705 and 1675  $\text{cm}^{-1}$  did not disappear. These observations show that the decomposition product of title compound is glycolurilene-3 (**5**).

On the basis of above-mentioned experiments, the mechanism of the initial stage of decomposition reaction for the title compound could be expressed by Scheme 2.

**Scheme 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 decomposition reaction for the title compound, a multiple heating method<sup>5</sup> (Kissinger's method) was employed. From the original data in Table 1, the apparent activation energy  $E_a$  was determined to be 218.9  $\text{kJ}\cdot\text{mol}^{-1}$ . The pre-exponential constant  $A$  is  $10^{19.74}\text{ s}^{-1}$ . The linear correlation coefficient  $r_k$  is 0.9296. The value of  $E_a$  obtained by Ozawa's method<sup>6</sup> is 216.5

$\text{kJ}\cdot\text{mol}^{-1}$ . The value of  $r_o$  is 0.9344.

**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 ( $\beta$ )

$\beta/(\text{ }^{\circ}\text{C}\cdot\text{min}^{-1})$	$T_p/^\circ\text{C}$
1.1538	241.00
2.0689	243.00
5.5000	245.00
10.909	257.00
22.667	268.00

In order to obtain the values of  $E_a$ ,  $A$  and the most probable kinetic model function from a single non-isothermal DSC curve, the integral Eq. (1),<sup>7</sup> differential Eq. (2)<sup>7</sup> and exothermic rate Eq. (3)<sup>7</sup> were employed.

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

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

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

where  $f(\alpha)$  and  $G(\alpha)$  are the differential and integral model functions, respectively,  $dH_t/dt$  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  $t$ ,  $\alpha$  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,

$$\frac{d\alpha}{dT} = \frac{1}{H_0 \beta} \frac{dH}{dt}$$

Thirty types of kinetic model functions in Ref. 8 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>7</sup> The values of  $E_a$  and  $A$ , corresponding to the probable kinetic model function (No. 7) of the integral method selected by the maximal value of  $r$  (0.9889) are 993.9  $\text{kJ}\cdot\text{mol}^{-1}$  and  $10^{96.03}\text{ s}^{-1}$ , respectively. The values of  $E_a$  and  $A$ , corresponding to the probable kinetic model function (No. 7) of the differen-

**Table 2** Data of the title compound determined by DSC<sup>a</sup>

Data point	$T_i/\text{K}$	$\alpha_i$	$(dH_i/dt)_i/(\text{mJ}\cdot\text{s}^{-1})$	$(da/dt)_i/\text{K}^{-1}$
1	511.2	0.0704	0.7196	0.0303
2	513.2	0.1268	1.004	0.0422
3	514.2	0.1761	1.490	0.0627
4	514.7	0.2183	1.757	0.0740
5	515.2	0.2606	2.226	0.0937
6	516.2	0.3521	2.761	0.1162
7	517.2	0.3803	3.565	0.1500
8	517.7	0.4507	4.485	0.1887
9	518.3	0.6690	5.908	0.2486

<sup>a</sup>  $T_0=505.2\text{ K}$ ;  $H_0=713.0\text{ mJ}$ ;  $\beta=0.03333\text{ K}\cdot\text{s}^{-1}$ .

tial method selected by the maximal value of  $r$  (0.9935) are  $1008\text{ kJ}\cdot\text{mol}^{-1}$  and  $10^{97.57}\text{ s}^{-1}$ , respectively. These values of  $E_a$  and  $A$  are not in the ordinary range of the thermal decomposition kinetic parameters for energetic materials [ $E_a=80\text{--}250\text{ kJ}\cdot\text{mol}^{-1}$  and  $\log(A/\text{s}^{-1})=7\text{--}30$ ], belonging to reasonable kinetic parameters.

In order to obtain the reasonable kinetic parameters by the exothermic rate Eq. (3), we took the minimal values of the evaluation functions  $\Omega(E, A, \dots)$

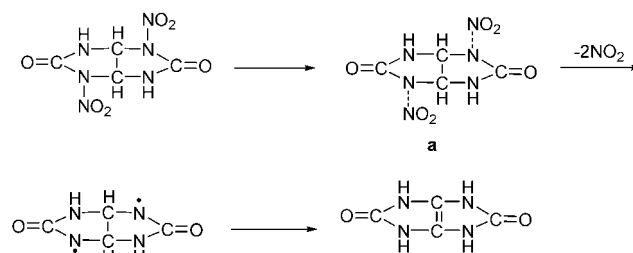
$$\Omega = \sum_{i=1}^l \left\{ \ln \left( \frac{dH_t}{dt} \right) - \ln [AH_0 f(\alpha_i)] \right. \\ \left. \left[ 1 + \frac{E_a}{RT_i} \left( 1 - \frac{T_0}{T_i} \right) \right] \right\} + \frac{E_a}{RT_i} \quad (4)$$

Once the value of  $E$  has been calculated from  $\partial \Omega / \partial E = 0$ , the corresponding values of  $A$ , and  $n$ ,  $m$  and  $k$  in the forms of  $f(\alpha)$  listed in Ref. 9 can then be obtained from the normal equations,  $\partial \Omega / \partial A = 0$ ,  $\partial \Omega / \partial n = 0$ ,  $\partial \Omega / \partial m = 0$  and  $\partial \Omega / \partial k = 0$ . In the iterative computation process of combined dichotomous and least-squares methods, we took  $AA=10^{-1}$ ,  $BB=10^{10}$ ,  $H=50.0$ ,  $E_1=10^{-10}$  and  $E_2=10^{-5}$ , where  $E$  is the root of the equation  $\partial \Omega / \partial E = 0$ ,  $AA$  and  $BB$  is the root interval of the equation  $\partial \Omega / \partial E = 0$ ,  $H$  is the step size, and  $E_1$  and  $E_2$  are two constants of the control precision. When the value of a certain point on the left side of the equation  $\partial \Omega / \partial E = 0$  is less than  $E_1$  or half of the small interval length is less than  $E_2$ , this point or the intermediate point of the small interval is the solution of the equation  $\partial \Omega / \partial E = 0$ . By substitution of the original data in Table 2, and fifteen forms of  $f(\alpha)$  in Ref. 9, into all the normal equations, the corresponding values of  $E$  of  $207.0\text{ kJ}\cdot\text{mol}^{-1}$  and  $A$  of  $10^{18.49}\text{ s}^{-1}$  and the probable empirical mechanism function  $\alpha^{0.526}$  are obtained by the method of logical choices.<sup>7</sup> 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. Therefore, we conclude that the kinetic equation of thermal decomposition of the title compound is

$$d\alpha/dT = 10^{19.98} \alpha^{0.526} e^{-2.49 \times 10^4/T}$$

The value of  $E_a$  approached the dissociation energy of the N-NO<sub>2</sub> bond ( $229.9\text{ kJ}\cdot\text{mol}^{-1}$ ),<sup>10</sup> indicating that the activated complex **a** as shown in Scheme 3 could be formed during decomposition.

**Scheme 3**

The value  $T_{po}$  of the peak temperature  $T_p$  corresponding to  $\beta \rightarrow 0$  obtained by Eq. (5) taken from Ref. 11 is  $242.24\text{ }^\circ\text{C}$ .

$$T_{pi} = T_{po} + b\beta_i + c\beta_i^2 + d\beta_i^3, \quad i=1\text{--}5 \quad (5)$$

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

The critical temperature of thermal explosion  $T_b$  obtained from Eq. (6) taken from Ref. 11 is  $252.87\text{ }^\circ\text{C}$ .

$$T_b = \frac{E_0 - \sqrt{E_0^2 - 4E_0RT_{po}}}{2R} \quad (6)$$

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  $T=T_{po}$ ,  $E=E_a$  and  $A=A_k$  obtained by Eqs. (7), (8) and (9) are  $128.4\text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ ,  $218.9\text{ kJ}\cdot\text{mol}^{-1}$  and  $152.7\text{ kJ}\cdot\text{mol}^{-1}$ , respectively.

$$A = \frac{k_B T}{h} e^{\Delta S^\ddagger/R} \quad (7)$$

$$A \exp(-E_a/RT) = \frac{k_B T}{h} \exp\left(\frac{\Delta S^\ddagger}{R}\right) \exp\left(-\frac{\Delta H^\ddagger}{RT}\right) \quad (8)$$

$$\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger \quad (9)$$

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

## Conclusions

The kinetics and mechanism of the exothermic decomposition reaction for the title compound have been investigated. The mechanism of the initial stage of decomposition reaction could be expressed by the scheme shown in the text. The empirical kinetic model function in differential form, apparent activation energy and pre-exponential constant of the exothermic decomposition reaction are  $\alpha^{0.526}$ ,  $207.0 \text{ kJ}\cdot\text{mol}^{-1}$  and  $10^{18.49} \text{ s}^{-1}$ , respectively. The critical temperature of thermal explosion of the compound is  $252.87 \text{ }^\circ\text{C}$ . The values of  $\Delta S^\ddagger$ ,  $\Delta H^\ddagger$  and  $\Delta G^\ddagger$  of the reaction at  $T_{\text{po}}$  are  $128.4 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ ,  $218.9 \text{ kJ}\cdot\text{mol}^{-1}$  and  $152.7 \text{ kJ}\cdot\text{mol}^{-1}$ , respectively.

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