



Kinetics and mechanism of the exothermic first-stage decomposition reaction of 1,3-bis(2,2,2-trinitroethyl)-1,3-diazacyclopentanone-2

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Abstract

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 kinetic model function in differential form, apparent activation energy (E_a) and pre-exponential factor (A) of this reaction are $(1 - \alpha)^2$, $178.41 \text{ kJ mol}^{-1}$ and $10^{17.06} \text{ s}^{-1}$, respectively. The critical temperature of thermal explosion of the compound is 184.99°C . The values of ΔS^\ddagger , ΔH^\ddagger and ΔG^\ddagger of this reaction are $91.54 \text{ J mol}^{-1} \text{ K}^{-1}$, $176.86 \text{ kJ mol}^{-1}$ and $135.83 \text{ kJ mol}^{-1}$, respectively.
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1. Introduction

Cyclicnitrourea compounds with *N*-trinitroethyl groups have a greater density and a higher detonation velocity. Some of the compounds could be used as high explosives. 1,3-bis(2,2,2-trinitroethyl)-1,3-diazacyclopentanone-2 (**1**) is a typical cyclicnitrourea compound. The crystal density is 1.94 g cm^{-3} . The detonation velocity corresponding to density

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at 1.694 g cm^{-3} is about 7962 ms^{-1} . Therefore, it is very possible that the compounds are used as high explosive. Its thermal stability, the stability of hydrolysis and the relationship between the electronic structure and properties have been reported in previous papers [1–3]. 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

1,3-Bis(2,2,2-trinitroethyl)-1,3-diazacyclopentanone-2 (**1**) was prepared in Xian Modern Chemistry Research Institute. Its purity was 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 $10 \text{ }^\circ\text{C min}^{-1}$. 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 Shanghai Balance Instrument Factory, using Ni/Cr–Ni/Si thermocouple plate and working in static air with heating rates $1\text{--}20 \text{ }^\circ\text{C min}^{-1}$. DSC curves were obtained with a cell of aluminium (diameter $5 \text{ mm} \times 3 \text{ mm}$), whose side is rolled up. $\alpha\text{-Al}_2\text{O}_3$ was used as reference material. The sample mass is about 0.7 mg . The calorimetric sensitivities are ± 20.92 and $\pm 41.84 \text{ mJ s}^{-1}$. The heating rate was calculated according to the actual rising rate of temperature from $50 \text{ }^\circ\text{C}$ to the temperature at the end of the reaction. The precision of temperature was $0.25 \text{ }^\circ\text{C}$. The temperature and heat were calibrated using pure indium and tin powders. 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.

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 an endothermic peak begins at its melting point ($171.5 \text{ }^\circ\text{C}$) with summit peak at $173.0 \text{ }^\circ\text{C}$. Compound **1** decomposes partly before melting, and the melting is accompanied by decomposition. The so-called “melting point” of compound **1** is melting point of the mixture of the original compound **1** and its decomposition products. A major exothermic peak at $192.2 \text{ }^\circ\text{C}$ is due to decomposition of compound **1** in molten state. TG curve shows two-stage mass loss in which the second stage begins at about $217 \text{ }^\circ\text{C}$ and completed at $330 \text{ }^\circ\text{C}$ accompanied with 77% mass loss. It is in agreement with the theoretical value of the mass loss of 79.11%, corresponding to the loss of the two trinitroethyl groups attached to nitrogen atom on two sides of carbonyl group. Above $330 \text{ }^\circ\text{C}$ there is a slow steady mass loss due to decomposition of parent diazacyclopentanone.

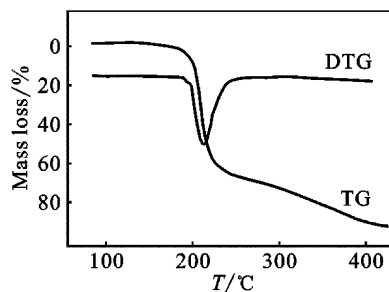


Fig. 1. TG-DTG curve for compound **1** at a heating rate of $10^{\circ}\text{C min}^{-1}$.

In order to understand the second-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 1600 and 1300 cm^{-1} . The characteristic absorption peak for the N-H group appears at 3300 cm^{-1} and those of the C-H group at 2860 and 1400 cm^{-1} do not disappear. The characteristic absorption peak of C=O at 1720 cm^{-1} has also been observed. These observations show that the parent ring of compound **1** did 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**, which is accordance with the results of degradation process of compound **1** obtained by means of mass spectrometer in [4].

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.

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**,

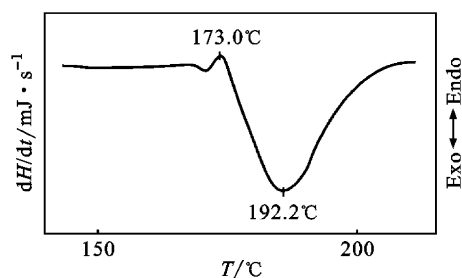
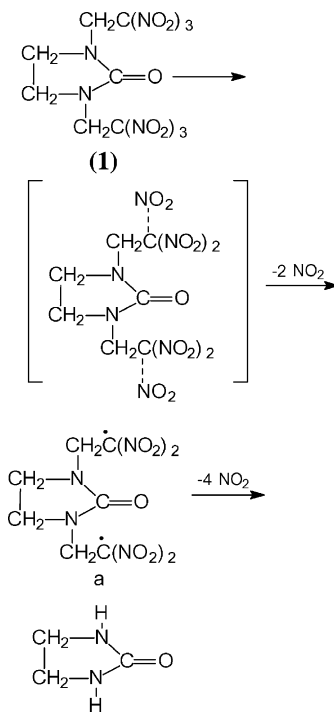


Fig. 2. DSC curve for compound **1** at a heating rate of $5^{\circ}\text{C min}^{-1}$.



Scheme 1.

a multiple heating method [5] (Kissinger's method) was employed. From the original data in Table 1, E_k is determined to be $176.86 \text{ kJ mol}^{-1}$ and $A 10^{17.75} \text{ s}^{-1}$. The linear correlation coefficient (r_k) is 0.9978. The values of E_0 and r_0 obtained by Ozawa's method [6] are $175.56 \text{ kJ mol}^{-1}$ and 0.9980, respectively.

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 [7].

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

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 ($^{\circ}\text{C min}^{-1}$)	T_p ($^{\circ}\text{C}$)
1.139	179.2
2.292	185.0
5.438	192.2
11.04	200.8
22.64	208.2

Table 2
Data of compound **1** determined by DSC^a

Data point	T_i (K)	α_i	$(dH_i/dt)_i$ (mJ s ⁻¹)	$(d\alpha/dT)_i$ (K ⁻¹)
1	469.2	0.0263	7.7153	0.01103
2	473.2	0.0766	9.9914	0.01428
3	477.2	0.1483	14.058	0.02010
4	480.2	0.2440	20.301	0.02902
5	485.2	0.2967	27.447	0.03923
6	487.2	0.3445	28.619	0.04091

^a $T_0 = 456.2$ K, $H_0 = 2098.7$ mJ, $\alpha = 0.3333$ °C s⁻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, α the conversion degree ($\alpha = H_t/H_0$), 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 the temperature (K) at time t

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

Thirty types of kinetic model function [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 [7].

The probable kinetic model functions of the integral and differential methods selected by the logical choice method [6] and satisfying ordinary range of the thermal decomposition kinetic parameters for energetic materials ($E = 80$ – 250 kJ mol⁻¹, $\log A = 7$ – 30 s⁻¹) are $f(\alpha) = (1 - \alpha)^2$ and $G(\alpha) = (1 - \alpha)^{-1} - 1$. The corresponding kinetic parameters are summarized in Table 3.

The values of E_a and A obtained by Eqs. (1) and (2) are in good agreement with the calculated values by Kissinger and Ozawa's method. The value of E_a approached the dissociation energy of the C–NO₂ bond (188.3 kJ mol⁻¹) [4], 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 [9] is 175.05 °C.

Table 3
Kinetic parameters obtained by the data in Table 2

No.	Eq.	$f(\alpha)$	E (kJ mol ⁻¹)	$\log A$ (s ⁻¹)	r	Q
1	(1)	$(1 - \alpha)^2$	211.38	20.50	0.9533	0.2970
2	(2)	$(1 - \alpha)^2$	178.41	17.06	0.9892	0.0464

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

where b , c and d are coefficients.

The critical temperature of thermal explosion (T_b) obtained from Eq. (4) taken from [9] is 184.99 °C.

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

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 (ΔS^\ddagger), enthalpy of activation (ΔH^\ddagger) and free energy of activation (ΔG^\ddagger) corresponding to $T = T_{p0}$, $E = E_k$ and $A = A_k$ obtained by Eqs. (5)–(7) are 91.54 J mol⁻¹ K⁻¹, 176.86 kJ mol⁻¹ and 135.83 kJ 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 × 10⁻²³ J K⁻¹) and h the Planck constant (6.626 × 10⁻³⁴ J s).

4. Conclusions

The kinetics and mechanism of the exothermic first-stage decomposition reaction for compound **1** have been investigated. The kinetic model function in differential form, apparent activation energy and pre-exponential constant of this reaction are $(1 - \alpha)^2$, 178.41 kJ mol⁻¹ and 10^{17.06} s⁻¹, respectively. The critical temperature of thermal explosion of the compound is 201.30 °C. The values of ΔS^\ddagger , ΔH^\ddagger and ΔG^\ddagger of the reaction in Scheme 1 at T_{p0} are 91.54 J mol⁻¹ K⁻¹, 176.86 kJ mol⁻¹ and 135.83 kJ mol⁻¹, respectively.

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