

文章编号:1006-9941(2005)01-0029-04

Kinetic Study on the Exothermic Decomposition Reaction of 2,4,6,8,10,12-Hexanitro-2,4,6,8,10,12-hexaazatricyclo[7·3·0·0^{3.7}] dodecane-5,11-dione

ZHAO Feng-qi¹, HU Rong-zu^{1,2}, YANG De-suo³, GAO Hong-xu¹,
LUO Yang¹, SONG Ji-rong^{2,4}, GAO Sheng-li², SHI Qi-zhen²

(1. Xi'an Modern Chemistry Research Institute, Xi'an 710065, China;

2. Shaanxi Key Laboratory of Physico-inorganic Chemistry, Department of Chemistry,
Northwest University, Xi'an 710069, China;

3. Department of Chem. and Chem. Eng. Baoji College of Arts and Science, Baoji 721007, China;

4. College of Chemical Engineering, Northwest University, Xi'an 710069, China)

Abstract: Under linear temperature increase condition the thermal behavior and kinetic parameters of the exothermic decomposition reaction of the title compound were studied by means of DSC. The results show that the empirical kinetic model function in differential form, apparent activation energy and pre-exponential constant of this reaction are $(1 - \alpha)^{-0.506}$, 155.5 kJ · mol⁻¹ and 10^{13.5} s⁻¹, respectively. The critical temperature of thermal explosion of the compound is 205.0 °C. The values of ΔS^\ddagger , ΔH^\ddagger and ΔG^\ddagger of this reaction are 6.0 J · mol⁻¹ · K⁻¹, 146.5 kJ · mol⁻¹ and 143.7 kJ · mol⁻¹, respectively.

Key words: physical chemistry; decomposition; 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazatricyclo [7 · 3 · 0 · 0^{3.7}] dodecane-5,11-dione; DSC; kinetics

CLC number: TJ55; O643

Document code: A

1 Introduction

2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazatricyclo[7·3·0·0^{3.7}] dodecane-5,11-dione is a typical cyclourea nitramine. Its crystal density is 2.07 g · cm⁻³. The detonation velocity corresponding to $\rho = 2.07 \text{ g} \cdot \text{cm}^{-3}$ is about 9700 m · s⁻¹. So it is the potential high explosive. Its preparation^[1], properties^[2~4] and hydrolytic behavior^[5,6] have been reported. In the present work, we report its kinetic parameters of the exothermic decomposition reaction studied with DSC, which 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.

Received Date: 2004-09-08; **Revised Date:** 2004-09-12

Project supported: by the Science and Technology Foundation of Shaanxi Key Laboratory of Physico-inorganic Chemistry (No. 29-3, 2001) and the Science and Technology Foundation of the National Defense Key Laboratory of Propellant and Explosive Combustion of China (No. 514550101, 2003)

Biography: ZHAO Feng-qi (1963-), male, professor, research fields: thermochemistry, thermal analysis and combustion property of energetic materials.
e-mail: npecc@21.cn.com

2 Experimental

2.1 Materials

The purified 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazatricyclo[7·3·0·0^{3.7}] dodecane-5,11-dione was prepared by Xi'an Modern Chemistry Research Institute. Its purity determined by HPLC was more than 99.5%. Sample was kept in a vacuum desiccator.

2.2 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⁻¹. The α -Al₂O₃ was used as reference material in the DSC measurements. DSC curves obtained under the same conditions overlapped with each other, indicating that the reproducibility of tests was satisfactory.

3 Results and discussion

3.1 Analysis of kinetic data

Typical DSC curve for the compound is shown in

Fig. 1. DSC curve shows that only one exothermic peak. 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 compound, a multiple heating method^[7] (Kissinger's method) was employed. From the original data in Table 1, the apparent activation energy (E_k) is determined to be $146.5 \text{ kJ} \cdot \text{mol}^{-1}$. The pre-exponential constant (A_k) is $10^{13.3} \text{ s}^{-1}$. The linear correlation coefficient (r_k) is 0.9812. The value of E_o obtained by Ozawa's method^[8] is $147.0 \text{ kJ} \cdot \text{mol}^{-1}$. The value of r_o is 0.9830.

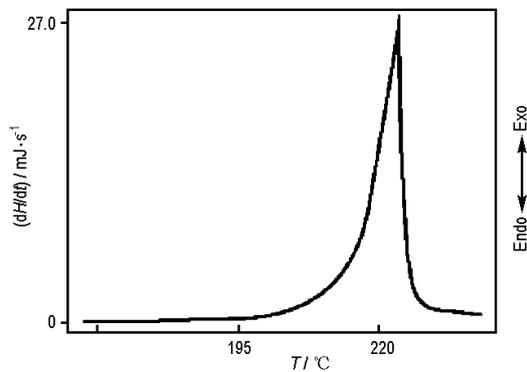


Fig. 1 DSC curve for the title compound at a heating rate of $5 \text{ }^\circ\text{C} \cdot \text{min}^{-1}$

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

$\beta/^\circ\text{C} \cdot \text{min}^{-1}$	$T_p/^\circ\text{C}$
0.9224	195
1.0345	204
2.1429	212
5.6000	221
10.427	228
20.830	239

In order to obtain the values of E_a , A and the most probable kinetic function from a single non-isothermal DSC curve, the integral Eq. (1)^[9], differential Eq. (2)^[9] and exothermic rate Eq. (3)^[9] were employed.

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

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

$$\ln\left(\frac{dH_t}{dt}\right)_i =$$

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

where $f(\alpha)$ and $G(\alpha)$ are the differential and integral model function, respectively, dH_t/dt is the exothermic heat flow at time t , H_0 is the total heat effect (corresponding to the global area under the DSC curve), H_t is the reaction heat at a certain time (corresponding to the partial area under the DSC curve), T_i is the temperature (K) at time t , α is the conversion degree ($\alpha = H_t/H_0$), T_0 is the initial point at which DSC curve deviates from the baseline, R is the gas constant, $\frac{d\alpha}{dT} = \frac{1}{H_0\beta} \frac{dH}{dt}$.

Thirty types of kinetic model function in Ref. [9] 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) are obtained by the linear least-squares and iterative methods^[9]. The values of E_a and A , corresponding to the probable kinetic model functions (No. 7 and 27) selected by the maximal value of r (0.9934) and the minimal value of Q (0.0276) with the integral method are $399.1 \text{ kJ} \cdot \text{mol}^{-1}$ and $10^{38.1} \text{ s}^{-1}$, and $-8.07 \text{ kJ} \cdot \text{mol}^{-1}$ and $10^{-3.61} \text{ s}^{-1}$, respectively. The values of E_a and A , corresponding to the probable kinetic model functions (No. 7 and 27) selected by the maximal value of r (0.9920) and Q (0.1862) with the differential method are $400.9 \text{ kJ} \cdot \text{mol}^{-1}$ and $10^{38.4} \text{ s}^{-1}$, and $37.0 \text{ kJ} \cdot \text{mol}^{-1}$ and $10^{1.11} \text{ s}^{-1}$, respectively. These values of E_a and A are not in the ordinary range of the thermal decomposition kinetic parameters for energetic materials ($E_a = 80 \sim 250 \text{ kJ} \cdot \text{mol}^{-1}$ and $\log A = 7 \sim 30 \text{ s}^{-1}$), 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 function $\Omega(E, A, \dots)$ (obtained from Eq. (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. [6] 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 take $AA=10^{-1}$, $BB=10^{10}$, $H=50.0$, $E_1=10^{-10}$ 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

$$\Omega = \sum_{i=1}^l \left\{ \ln\left(\frac{dH_i}{dt}\right)_i - \ln\{AH_0f(\alpha_i)[1 + \frac{E_a}{RT_i}(1 - \frac{T_0}{T_i})]\} + \frac{E_a}{RT_i} \right\} \quad (4)$$

Table 2 Data of the title compound determined by DSC¹⁾

data point	T_i/K	α_i	$(dH_i/dt)_i$ / $\text{mJ} \cdot \text{s}^{-1}$	$(d\alpha/dT)_i$ / K^{-1}
1	468.2	0.0249	0.8368	0.4535
2	470.2	0.0386	1.1213	0.6077
3	473.2	0.0522	1.5062	0.8163
4	477.2	0.0726	1.8744	1.016
5	478.2	0.0975	2.3932	1.297
6	480.2	0.1451	3.3137	1.796
7	483.2	0.1950	4.6861	2.540
8	487.2	0.2721	6.8618	3.719
9	490.2	0.3878	10.209	5.533
10	491.2	0.5669	16.267	8.816
11	494.2	0.8390	27.330	14.81

Note: 1) $T_0=452.2$ K; $H_0=2214.2$ mJ; $\beta=0.08333$ K \cdot s⁻¹

The value (T_{p0}) of the peak temperature (T_p) corresponding to $\beta \rightarrow 0$ obtained by Eq. (5) taken from Ref. [11] is 192.1 °C.

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

where b , c and d are coefficients.

The critical temperature of thermal explosion (T_b) obtained from Eq. (6) taken from Ref. [11] is 205.0 °C.

$$T_b = \frac{E_o - \sqrt{E_o^2 - 4E_oRT_{p0}}}{2R} \quad (6)$$

where R is the gas constant (8.314 J \cdot mol⁻¹ \cdot K⁻¹), E_o 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 $T=T_{p0}$, $E=E_A$ and $A=A_k$ obtained by

$\partial\Omega/\partial E=0$. By substitution the original data in Table 2, and fifteen forms of in Ref. [10], into all the normal equations, the corresponding values of E of 155.5 kJ \cdot mol⁻¹ and A of $10^{13.5}$ s⁻¹ and the probable empirical mechanism function $(1-\alpha)^{-0.506}$ are obtained by the method of logical choices^[9]. 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, it was concluded that the kinetic equation of thermal decomposition of the title compound is $d\alpha/dT = 10^{14.6} (1-\alpha)^{-0.506} e^{-1.87 \times 10^4/T}$.

Eqs. (7), (8) and (9) are 6.0 J \cdot mol⁻¹ \cdot K⁻¹, 146.5 kJ \cdot mol⁻¹ and 143.7 kJ \cdot 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 is the Planck constant.

4 Conclusions

The thermal behavior and kinetic parameters [apparent activation energy (E_a) and pre-exponential constant (A)] of the exothermic decomposition reaction of the title compound was investigated. The kinetic model function in differential form of this reaction is $(1-\alpha)^{-0.506}$. The values of E_a and A are 155.5 kJ \cdot mol⁻¹ and $10^{13.5}$ s⁻¹, respectively. The critical temperature of thermal explosion of the compound is 205.0 °C. The values of ΔS^\ddagger , ΔH^\ddagger and ΔG^\ddagger of the reaction at T_{p0} are 6.0 J \cdot mol⁻¹ \cdot K⁻¹, 146.5 kJ \cdot mol⁻¹ and 143.7 kJ \cdot mol⁻¹ respectively.

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2,4,6,8,10,12-六硝基-2,4,6,8,10,12-六氮杂三环 [7·3·0·0^{3.7}] 十二烷酮-5,11 放热分解反应的动力学研究

赵凤起¹, 胡荣祖^{1,2}, 杨得锁³, 高红旭¹, 罗 阳¹,
陈三平², 赵宏安², 宋纪蓉^{2,4}, 高胜利², 史启祯²

- (1. 西安近代化学研究所, 陕西 西安 710065;
2. 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;
3. 宝鸡文理学院化学化工系, 陕西 宝鸡 721007;
4. 西北大学化工学院, 陕西 西安 710069)

摘要: 用 DSC 研究了标题化合物在线性升温条件下的热行为和放热分解反应的动力学参数。结果表明: 该反应的微分形式的经验动力学模式函数、表观活化能和指前因子分别为 $(1 - \alpha)^{-0.506}$, $155.5 \text{ kJ} \cdot \text{mol}^{-1}$ 和 $10^{13.5} \text{ s}^{-1}$, 标题化合物的热爆炸临界温度为 $205.0 \text{ }^\circ\text{C}$ 。该反应的 ΔS^\ddagger , ΔH^\ddagger 和 ΔG^\ddagger 分别为 $6.0 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$, $146.5 \text{ kJ} \cdot \text{mol}^{-1}$ 和 $143.7 \text{ kJ} \cdot \text{mol}^{-1}$ 。

关键词: 物理化学; 热分解; 2,4,6,8,10,12-六硝基-2,4,6,8,10,12-六氮杂三环 [7·3·0·0^{3.7}] 十二烷酮-5,11; DSC; 动力学;

中图分类号: TJ55; O643

文献标识码: A

* 读者·作者·编者 *

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