研究简报

2,4,6-三硝基间苯二酚钡一水化合物的热分解动力学

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Thermal Decomposition Kinetics of Barium 2,4,6-trinitroresorecinate Monohydrate

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Studies of the non-isothermal decomposition of barium 2,4,6-trinitroresorecinate monohydrate, Ba(TNR)·H_2O, were carried out by means of TG-DTA, DSC and IR. The thermal decomposition mechanism and associated kinetics were investigated. The kinetic parameters were obtained from an analysis of the DSC curves by integral and differential methods. The most probable kinetic model function of the dehydration reaction of Ba(TNR)·H_2O was suggested by comparison of the kinetic parameters.

Keywords: **Ba(TNR)·H_2O** **DSC** **non-isothermal kinetics** **TG-DTA** **thermal decomposition**

0 Introduction

Barium 2,4,6-trinitroresorecinate monohydrate, Ba(TNR)·H_2O, has good detonating properties and is sensitive to flame. It can be used as initiating agent, igniter powder or delay powder. Its preparation[1], properties[1], crystal structure[1] and thermal behavior[2] have been reported. In the present work, we report its kinetic parameters and mechanism of thermal decomposition reaction studied with TG-DTA, IR and DSC. 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.

1 Experimental

1.1 Material

The single crystal of Ba(TNR)·H_2O used in this work was prepared by Shaanxi Applied Physics-Chemistry Research Institute. The single crystal with dimensions of 0.3 mm × 0.3 mm × 0.1 mm was selected for the experiment.

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1.2 Equipment and Conditions

TG-DTA and DSC curves under static air condition were obtained using a LCT-1 thermal analyzer made by the Beijing Optical Instrument Factory and a CDR-1 differential scanning calorimeter (Shanghai Tianping Instrument Factory, China) with an aluminium cell. The conditions of TG-DTA were as follows: sample mass, about 1 mg; heating rate, 5 ℃·min^{-1}; sensitivity: 2 mg(TG), 25 μV (DTA) and 5 mV(temperature). The conditions of the DSC analyses were: sample mass, about 0.5 mg; heating rates, 2, 5, 10 and 20 K·min^{-1}, respectively; calorimetric sensitivities, ±20.92 and ±41.84 mJ·s^{-1}; reference sample, α-Al_2O_3. Heating rate is calculated according to the actual rate of temperature rise from 50 ℃ to the temperature at the end of decomposition. The precision of temperature was 0.25 K.

The thermal decomposition process of the title compound under the condition of flowing N_2 gas was studied on a TGA-DTA and DSC apparatus (TA, USA). The conditions of TGA-DTA were as follows: sample mass, about 0.5 mg; heating rate, 10 ℃·min^{-1}; atmosphere, a flowing rate of N_2 gas of 120 mL·min^{-1}; reference sample, α-Al_2O_3. The conditions of DSC were as follows: sample mass, about 1mg; heating rates, 2, 5, 10 and 15 K·min^{-1}; atmosphere, a flowing rate of N_2 gas of 60 mL·min^{-1}; reference sample, α-Al_2O_3.

The infrared spectra of the title compound before and after thermal decomposition were recorded in KBr discs on a Perkin-Elmer Model 180 IR spectrophotometer.

2 Results and Discussion

2.1 Mechanism of the Thermal Decomposition of the Title Compound Under Static Air Conditions

The TG-DTA and DSC curves of the title compound under static air conditions are shown in Figs.1 and 2, respectively. The DTA and DSC curves in Figs. 1 and 2 show that there are one endothermic and two exothermic processes between 204.5 ℃ and 507 ℃. In

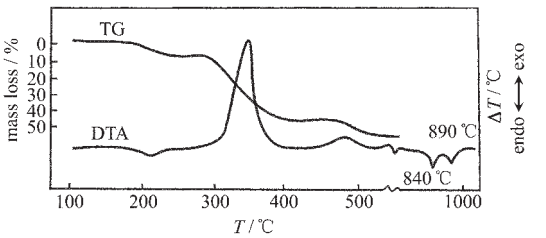

Fig.1 TG-DTA curve for the title compound at a heating rate of 5 ℃·min^{-1}

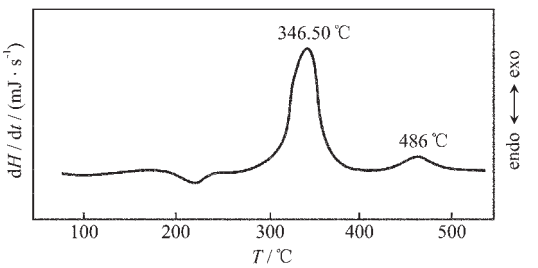

Fig.2 DSC curve for the title compound at a heating rate of 10 ℃·min^{-1}

Table 1, the initial and final temperatures of the thermal decomposition processes and the mass losses observed between these temperatures in TG curve are given. The enthalpy of the dehydration reaction (ΔH_{deh}) and enthalpy of the major exothermic decomposition reaction (ΔH_{dec}) are also listed in Table 1. The characteristic absorption peaks of the title compound and the residue formed after each DSC peak, and their tentative assignments are listed in Table 2. It can be seen from Figs.1 and 2, and Tables 1 and 2 that the endothermic process results in a loss of one water molecule. Further decomposition of the dehydrated compound, Ba (TNR) would occur on heating. The characteristic absorption peaks of the residue formed after the first exothermic peak appear at 3 400, 2 160, 1 600, 1 400, 870 and 770 cm^{-1}, indicating that the decomposition residue for this stage is a noncrystalline inorganic mixture. The characteristic absorption peaks of the residue formed after the second exothermic peak at 1 430, 1 050, 855 and 690 cm^{-1} are assigned to $BaCO_3$. The formation of $BaCO_3$ from the original sample should be accomplished with a theoretical overall mass loss of 50.00 %. This value is in agreement with the experimental value of 50.50 %. Two endothermic peak at about 840 ℃ and 890 ℃ in Fig.1

Table 1 Data on the Thermal Decomposition of Ba(TNR)·H_2O Obtained by TG and DSC

decomposition stage	temperature range / ℃	mass loss / %	ΔH_{deh} / (J·g^{-1})[a]	ΔH_{dec} / (J·g^{-1})[b]
	TG	obs(calc.)		
Ba(TNR)·H_2O				
$\xrightarrow{-H_2O}$ Ba(TNR)	204.5~245.5	4.60(4.52)	182.22±2.26[c]	
$\xrightarrow{-3NO_2}$ noncrystalline inorganic mixture	334~398	34.7(34.6)		193 6.6±80.5[d]
$\longrightarrow$ $BaCO_3$	398~507	$\frac{10.7}{50.00}$ $\frac{(11.38)}{50.50}$		

a: ΔH_{deh}, Enthalpy of the dehydration reaction; b: ΔH_{dec}, Enthalpy of the major exothermic decomposition reaction; c: Averages of seven experiments; d: Averages of five experiments.

are assigned to the decomposition of $BaCO_3$, which is in agreement with the DTA results of pure $BaCO_3$ in static air reported in Ref[3].

On the bases of experimental and calculated results in Tables 1 and 2, the thermal decomposition mechanism of the title compound could be shown as scheme 1.

$$\text{Ba(TNR)}\cdot H_2O \xrightarrow[204.5\sim245.5\ ℃]{-H_2O} \text{Ba(TNR)} \xrightarrow[344\sim398\ ℃]{-3NO_2} \text{noncrystalline inorganic compound} \xrightarrow[398\sim507\ ℃]{} BaCO_3$$

Scheme 1

Table 2 IR Data of Ba(TNR)·H_2O and Its Decomposition Products

temp. / ℃	IR data / cm^{-1}	tentative assignments
RT	3 470; 1 630	H_2O
	1 580; 1 550; 1 520; 1 300	Ar-NO_2
	3 100; 1 470; 1 420; 785; 700	Ar
	1 220	Ar-O
246.0	3 050; 1 500; 1 410; 790; 690	Ar
	1 570; 1 320	Ar-NO_2
	1 230	Ar-O
398	3 400(s,b); 2 160(s); 1 600(s,b)	inorganic compound
	1 400(s,b); 870; 770(w)	
507	1 430(s,b); 1 050(w); 855(m);	$BaCO_3$
	690(m)	

Note: b=broad, m=medium, s=strong, w=weak.

2.2 Analysis of Kinetic Data

The typical TG-DTA and DSC curves for the thermal decomposition of the title compound under the condition of flowing N_2 gas are shown in Figs.3 and 4. The TG curve consists of two-stage mass loss process. The DTA and DSC curves consist of one endothermic peak of the dehydration reaction of the title compound and one exothermic decomposition peaks of the dehydrated compound Ba(TNR).

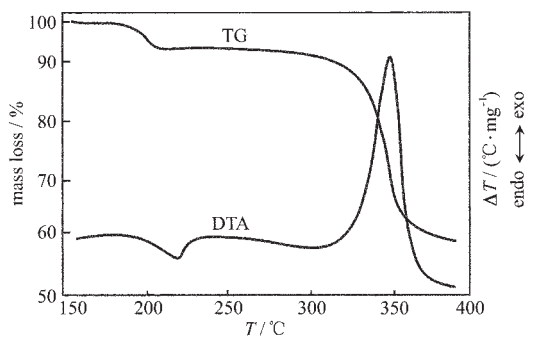

Fig.3 TG-DTA curve for the title compound at a heating rate of 10 ℃·min^{-1} and a flowing rate of N_2 gas of 120 mL·min^{-1}

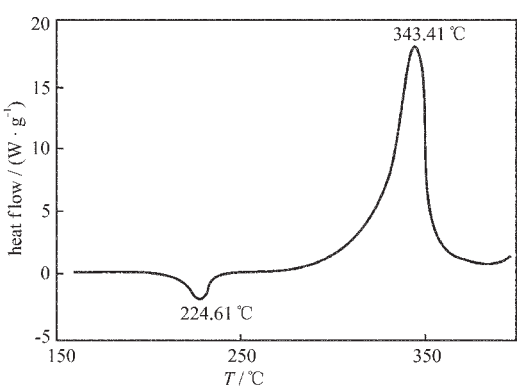

Fig.4 DSC curve for the title compound at a heating rate of 10 ℃·min^{-1} and a flowing rate of N_2 gas of 60 mL·min^{-1}

In order to obtain the kinetic parameters [apparent activation energy (E_a) and pre-exponential constant (A)] of the dehydration reaction and the major exothermic decomposition reaction for the title compound, a multiple heating method[4] (Kissinger′s method) was employed. From the original data in Tables 3 and 4, E_k of the dehydration reaction is determined to be 127.6 kJ·mol^{-1} and $A_k=10^{11.38}$ s^{-1}. The linear correlation coefficient (r_k) is 0.995 8. The values of E_0 and r_0 obtained by Ozawa′s method[5] are 129.1 kJ·mol^{-1} and 0.996 4, respectively. For the exothermic decomposition reaction, E_k is determined to be 163.2 kJ·mol^{-1} and $A_k=10^{11.75}$ s^{-1}. The value of r_k is 0.999 6. The values of E_0 and r_0 are 164.8 kJ·mol^{-1} and 0.999 7, respectively. These values of E_k and A_k for the major exothermic decomposition of the title compound under static air conditions are 178.50 kJ·mol^{-1} and $10^{13.01}$ s^{-1} respectively (see Table 4). It can be seen from Table 3 that the value of E_0 obtained from the relationship of $\ln\beta$ vs T_e^{-1} for the dehydration reaction is in agreement with the calculated value obtained from the relationship of $\ln\beta_i$ vs T_p^{-1}, indicationg that the value of E_0 of 122.6 kJ·mol^{-1} for the dehydration reaction is acceptable.

Table 3　Calculated Values of the Kinetic Parameters for the Endothermic and Exothermic Decomposition for the Title Compond Determined from the DSC Curves at Various Heating Rates and a Flowing Rate of N_2 Gas of 60 mL·min^{-1} [a]

β / (K·min^{-1})	T_e / ℃	E_0 / (kJ·mol^{-1})	r_0	T_p / ℃	E_k / (kJ·mol^{-1})	lg(A_k /s^{-1})	r_k	E_0 / (kJ·mol^{-1})	r_0	T_{eo} / ℃	T_b^b / ℃	T_{po} / ℃	T_b^c / ℃
dehydrated reaction													
2.0	188.08	117.6	0.994 9	203.14	127.6	11.38	0.995 8	129.1	0.996 4				
5.0	199.50			213.73									
10.0	213.65			224.61									
20.0	221.97			237.16									
mean: E_0=(117.6+127.6)/2=122.6(kJ·mol^{-1})													
exothermic decomposition reation													
2.0	299.80	166.1	0.999 1	315.61	163.2	11.75	0.999 6	164.8	0.999 7	283.07	299.48	298.75	316.28
5.0	315.69			332.05									
10.0	325.72			343.41									
20.0	338.59			356.84									
mean: E_0=(166.1+164.8)/2=165.45(kJ·mol^{-1})													

a: β, Heating rate; T_e, onset temperature in the DSC curve; T_p, maximum peak temperature; T_{eo}, the value (T_{eo}) of the onset temperature (T_e) corresponding to $\beta \to 0$ obtained by Eq.(**8**); T_b, critical temperature of thermal explosion; E, apparent activation energy; A, preexponential constant; r, linear correlation coefficient; subscript k, data obtained by Kissinger′s method; subscript 0, data obtained by Ozawa′s method.

b: The value of T_b obtained by the value of T_{eo} in Eq.(**8**).

c: The value of T_b obtained by the value of T_{po} in Eq.(**8**).

Table 4　Values of T_b and Kinetic Parameters for the Major Exothermic Decomposition Reaction of the Title Compound Determined from the DSC Curves at Various Heating Rates under Static Air Conditions[a]

β / (K·min^{-1})	T_p / ℃	T_{po} / ℃	Kissinger′s method			Ozawa′s method		T_b / ℃
			E_k / (kJ·mol^{-1})	lg(A_k / s^{-1})	r_k	E_0 / (kJ·mol^{-1})	r_0	
2.028 6	320.25	306.28	178.5	13.01	0.999 8	179.4	0.999 8	322.74
5.121 2	334.75							
10.631	346.50							
21.250	359.25							

a: The meanings of symbols in Table 4 are the same as those in Table 3.

The integral Eqs.(**1**)[6] and (**2**) [7], differential Eq. (**3**) [8] 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

$$\lg[G(\alpha)]=\lg(\frac{AE_a}{\beta R})-2.315-0.4567\frac{E_a}{RT} \quad (\mathbf{1})$$

$$\ln\left[\frac{G(\alpha)}{T^2\left(1-\frac{2RT}{E_a}\right)}\right]=\ln\frac{AR}{\beta E_a}-\frac{E_a}{RT} \quad (\mathbf{2})$$

$$\ln(\frac{dH}{dt})=\ln\{AH_0f(\alpha)[1+\frac{E_a}{RT}(1-\frac{T_0}{T})]\}-\frac{E_a}{RT} \quad (\mathbf{3})$$

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 ($\alpha=H_t/H_0$), 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 at time t, $\frac{d\alpha}{dT}=\frac{1}{H_0\beta}\frac{dH}{dt}=\frac{1}{\beta}\frac{d\alpha}{dt}$.

Forty-one types of kinetic model function[9] and the data in Tables 5, 6, 7 and 8 are put into Eqs.(**1**) and (**2**) for calculation ,respectively. The values of E_a, A, linear correlation coefficient (r), standard mean square deviation (Q) and believable factor (d) (where $d=(1-\alpha)Q$ are obtained by the linear least-squares and iterative methods[6]. The probable kinetic model functions of two integral methods selected by the better values of r, Q and d and satisfying ordinary range of the thermal decomposition kinetic parameters for energetic materials (E=80~250 kJ·mol^{-1} and lg$A$=7~30 s^{-1}) are respectively $[-\ln(1-\alpha)]^{\frac{1}{4}}$ for the dehydration reaction and $[-\ln(1-\alpha)]^{\frac{1}{2}}$ for the exothermic decomposition reaction, indicating that the reaction mechanism of the dehydration and exothermic decompostion processes of the title compound is classified as nucleation and growth, and the mechanism function is the Avrami-Erofeev equation with $n=\frac{1}{4}$ for the former and $n=\frac{1}{2}$ for the latter. The calculated values of the kinetic parameters of the dehydration reaction corresponding to this probable kinetic model function are listed in Tables 9 and 10. In order to obtain the kinetic parameters of the exothermic decomposition reaction by differential equation (**3**), we took the minimal values of the evaluation functions Ω (E, A, ...):

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

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 Table 11 can then

Table 5 Basic Data of the Dehydration Process of Ba(TNR)·H$_2$O Determined by DSC [a]

data point	T_i / K	α_i	$(dH/dt)_i$ / (mJ·s^{-1})	$(d\alpha/dt)_i\times10^4$ / s^{-1}	$(d\alpha/dT)_i\times10^3$ / K^{-1}
1	460.15	0.002 0	0.044 4	4.919	14.67
2	462.15	0.006 9	0.054 1	5.993	17.88
3	464.15	0.015 1	0.066 3	7.345	21.91
4	466.15	0.028 3	0.081 5	9.028	26.93
5	468.15	0.050 0	0.099 7	11.04	32.95
6	470.15	0.085 4	0.131 3	14.55	43.39
7	472.15	0.141 5	0.181 8	20.14	60.08
8	474.15	0.239 8	0.267 5	29.63	88.41
9	476.15	0.399 7	0.365 4	40.48	120.8
10	478.15	0.608 0	0.422 6	46.82	139.7
11	480.15	0.821 7	0.384 3	42.57	127.0
12	482.15	0.962 8	0.220 7	24.45	72.94
13	484.15	0.998 0	0.111 3	12.33	36.78

a: T_0=448.15 K; H_0=90.27 mJ; β=0.0333 K·s^{-1}.

Table 6　Basic Data of the Dehydration Process of Ba(TNR)·H_2O Determined by DSC [a]

data point	T_i / K	α_i	$(dH/dt)i$ / (mJ·s^{-1})	$(d\alpha/dt)_i\times10^4$ / s^{-1}	$(d\alpha/dT)_i\times10^3$ / K^{-1}
1	477.15	0.001 2	0.021 6	3.760	2.255
2	479.15	0.004 8	0.028 1	4.891	2.934
3	481.15	0.010 1	0.038 5	6.701	4.019
4	483.15	0.018 5	0.054 4	9.469	5.679
5	485.15	0.032 3	0.072 2	12.57	7.538
6	487.15	0.047 5	0.093 8	16.33	7.793
7	489.15	0.071 0	0.130 8	22.77	13.66
8	491.15	0.104 0	0.183 8	31.99	19.19
9	493.15	0.150 9	0.262 6	45.71	27.42
10	495.15	0.220 0	0.390 7	68.01	40.79
11	497.15	0.323 3	0.578 3	100.7	60.37
12	499.15	0.469 9	0.770 3	134.1	80.42
13	501.15	0.649 6	0.882 1	153.5	92.09
14	503.15	0.836 7	0.828 0	144.1	86.44
15	505.15	0.985 3	0.526 2	91.59	54.94

a: T_0=473.15 K; H_0=57.45 mJ; β=0.167 K·s^{-1}.

Table 7　Basic Data of the Dehydration Process of Ba(TNR)·H_2O Determined by DSC [a]

data point	T_i / K	α_i	$(dH/dt)_i$ / (mJ·s^{-1})	$(d\alpha/dt)_i\times10^4$ / s^{-1}	$(d\alpha/dT)_i\times10^3$ / K^{-1}
1	479.15	0.000 006	0.035 3	5.872	1.762
2	481.15	0.002 5	0.054 1	8.999	2.700
3	483.15	0.007 1	0.072 4	12.04	3.613
4	485.15	0.016 2	0.096 6	16.07	4.820
5	487.15	0.026 6	0.122 9	20.44	6.133
6	489.15	0.042 9	0.157 8	26.25	7.874
7	491.15	0.063 8	0.202 0	33.60	10.08
8	493.15	0.091 8	0.267 7	44.53	13.36
9	495.15	0.128 9	0.365 6	60.81	18.24
10	497.15	0.180 5	0.514 9	85.65	25.69
11	499.15	0.250 2	0.708 9	117.9	35.37
12	501.15	0.342 4	0.919 5	152.9	45.88
13	503.15	0.456 3	1.112	185.0	55.49
14	505.15	0.588 3	1.239	206.1	61.83
15	507.15	0.726 6	1.227	204.1	61.23
16	509.15	0.853 5	0.993 3	165.2	49.57
17	511.15	0.945 7	0.547 1	91.00	27.30
18	513.15	0.992 6	0.092 5	153.9	4.616

a: T_0=473.15 K; H_0=60.12 mJ; β=0.333 3 K·s^{-1}.

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 $\partial\Omega/\partial E=0$, $[AA, BB]$ 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 inter-

Table 8 Basic Data of the Exothermic Decomposition of $Ba(TNR)\cdot H_2O$ Determined by DSC [a]

data point	T_i / K	α_i	$(dH/dt)_i$ / (mJ·s^{-1})	$(d\alpha/dt)_i\times10^4$ / s^{-1}	$(d\alpha/dT)_i\times10^3$ / K^{-1}
1	529.15	0.000 06	0.002 4	0.014 0	0.041 9
2	532.15	0.000 7	0.011 6	0.067 5	0.202 4
3	535.15	0.002 3	0.019 5	0.113 4	0.340 3
4	538.15	0.004 8	0.031 0	0.180 3	0.541 0
5	541.15	0.008 4	0.044 4	0.258 3	0.774 8
6	544.15	0.013 4	0.058 4	0.339 7	1.019
7	547.15	0.019 5	0.076 6	0.445 6	1.337
8	550.15	0.027 4	0.100 3	0.583 5	1.750
9	553.15	0.037 1	0.124 6	0.724 8	2.174
10	556.15	0.048 8	0.161 1	0.937 2	2.811
11	559.15	0.063 5	0.204 9	1.192	3.576
12	562.15	0.081 2	0.260 2	1.514	4.541
13	565.15	0.103 4	0.337 4	1.963	5.888
14	568.15	0.130 8	0.438 4	2.550	7.650
15	571.15	0.165 2	0.562 4	3.272	9.814
16	574.15	0.208 3	0.740 1	4.305	12.91
17	577.15	0.264 2	0.985 5	5.733	17.20
18	580.15	0.337 2	1.338	7.784	23.35
19	583.15	0.434 6	1.832	10.66	31.97
20	586.15	0.563 2	2.385	13.87	41.62
21	589.15	0.717 6	2.605	15.15	45.46
22	592.15	0.862 2	1.912	6.934	33.36
23	595.15	0.948 1	0.718 5	4.180	12.54
24	598.15	0.977 8	0.115 5	0.671 9	2.015
25	561.15	0.988 9	0.029 2	0.169 9	0.509 5
26	564.15	0.994 8	0.009 9	0.057 6	0.172 8

a: T_0=529.15 K; H_0=1719.0 mJ; β=0.033 3 K·s^{-1}.

Table 9 Calculated Values of Kinetic Parameters of Dehydration Reaction for the Title Compound

β / (K·min^{-1})	$G(\alpha)$	$f(\alpha)$	Eq.(**1**)		Eq.(**2**)	
			E_a / (kJ·mol^{-1})	lg(A / s^{-1})	E_a / (kJ·mol^{-1})	lg(A / s^{-1})
2	$[-\ln(1-\alpha)]^{\frac{1}{4}}$	$4(1-\alpha)[-\ln(1-\alpha)]^{\frac{3}{4}}$	138.18[a]	10.71[a]	137.46[b]	10.65[b]
10	$[-\ln(1-\alpha)]^{\frac{1}{4}}$	$4(1-\alpha)[-\ln(1-\alpha)]^{\frac{3}{4}}$	120.71[c]	8.85[c]	118.77[d]	8.63[d]
20	$[-\ln(1-\alpha)]^{\frac{1}{4}}$	$4(1-\alpha)[-\ln(1-\alpha)]^{\frac{3}{4}}$	121.32[e]	9.10[e]	119.33[f]	8.87[f]
mean			E_a=125.96 kJmol^{-1}, lg(A / s^{-1})=9.47			

a: r=0.997 3, Q=0.004 7, d=0.000 1; b: r=0.996 9, Q= 0.027 4, d=0.000 08; c: r=0.990 8, Q=0.015 8; d=0.000 1;
d: r=0.989 5, Q=0.084 0, d=0.000 9; e: r=0.946 9, Q=0.164 0, d=0.008 7; f: r=0.939 9, Q=0.871 4, d=0.052 4.

val 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 the original data in Table 8 , and all the forms of $f(\alpha)$ in Table 11, into all the normal equations, the corresponding values of E and A and the probable empirical mechanism function

Table 10　Calculated Values of Kinetic Parameters of Exothermic Decomposition Reaction for the Title Compound

β / (K·min^{-1})	integral method						differntial method		
	$G(\alpha)$	$f(\alpha)$	Eq.(**1**)		Eq.(**2**)		Eq.(**3**)		
			E_a / (kJ·mol^{-1})	lg(A/s^{-1})	E_a / (kJ·mol^{-1})	lg(A/s^{-1})	$f(\alpha)$	E_a / (kJ·mol^{-1})	lg(A/s^{-1})
2	$[-\ln(1-\alpha)]^{\frac{1}{2}}$	$2(1-\alpha)[-\ln(1-\alpha)]^{\frac{1}{2}}$	151.98[a]	9.05[a]	150.43[b]	8.91[b]	$(1-\alpha)^{0.36}[1-\ln(1-\alpha)^{7.12}]$	151.09[c]	9.60[c]
			mean E_a=151.17 kJ·mol^{-1}, lg(A/s^{-1})=9.19						

a: r=0.972 4, Q=0.516 4, d=0.014 3; b: r=0.968 8, Q=2.275 0, d=0.085 7; c: r=0.967 7, Q=2.835 7, d=0.091 6.

are obtained by the method of logical choices[8]. The results are also summarized in Table 10. These values of E_a and A obtained from a single non-isothermal DSC curve are in agreement with the calculated values obtained by Kissinger′s method and Ozawa′s method. Comparing the kinetic parameters and the values of r, Q and d in Tables 10, we selected the kinetic model functon , $[-\ln(1-\alpha)]^{\frac{1}{2}}$.

Substituting $f(\alpha)$ with $4(1-\alpha)[-\ln(1-\alpha)]^{\frac{3}{4}}$, E_a with 125.96 kJ·mol^{-1}, β with 10 K·min^{-1} and A with $10^{9.47}$ s^{-1} in Eq.(**5**)

$$\frac{d\alpha}{dT}=\frac{A}{\beta}f(\alpha)\exp(-E_a/RT) \qquad (5)$$

we can establish the kinetic equation of the dehydration process of the title compound as follows

$$\frac{d\alpha}{dT}=10^{10.85}(1-\alpha)[-\ln(1-\alpha)]^{\frac{3}{4}}e^{-1.515\times10^4/T} \qquad (6)$$

Similarly, substituting $f(\alpha)$ with $2(1-\alpha)[-\ln(1-\alpha)]^{\frac{1}{2}}$, E_a with 151.17 kJ·mol^{-1}, β with 2 K·min^{-1} and A with $10^{9.19}$ s^{-1} in Eq.(**5**), the kinetic equation (**7**) of the exothermic decomposition process of the title compound is obtained:

$$\frac{d\alpha}{dT}=10^{10.97}(1-\alpha)[-\ln(1-\alpha)]^{\frac{1}{2}}e^{-1.818\times10^4/T} \qquad (7)$$

Under the condition of flowing N_2 gas, the values (T_{eo} and T_{po}) of the onset temperature (T_e) and the peak temperature (T_p) corresponding to $\beta \rightarrow 0$ obtained by Eq.(**8**) taken from Ref[10] using the data of T_e, T_p and β in Table 3 are 283.07 ℃ and 298.87 ℃, respectively.

$$T_{(e\text{ or }p)i}=T_{eo\text{ or }po}+b\beta_i+c\beta_i^2+d\beta_i^3,\quad i=1,2,3,4 \qquad (8)$$

where b, c and d are coefficients.

The values of the critical temperature of thermal explosion (T_b) obtained from Eq.(**9**) taken from Ref.[10] using the above-mentioned values of T_{eo} and T_{po}, and the value of E_0 in Table 3 are 299.48℃ and 316.28℃, respectively.

Table 11　Kinetic Functions Used for the Present Analysis

function No.	function form (differential form), $f(\alpha)$
1	$(1-\alpha)^n$
2	α^m
3	$[1-\ln(1-\alpha)]^k$
4	$\alpha^m(1-\alpha)^n$
5	$\alpha^m[1-\ln(1-\alpha)]^k$
6	$(1-\alpha)^n[1-\ln(1-\alpha)]^k$
7	$\alpha^m(1-\alpha)^n[1-\ln(1-\alpha)]^k$
8	$[-\ln(1-\alpha)]^k$
9	$\alpha^m[-\ln(1-\alpha)]^k$
10	$(1-\alpha)^n[-\ln(1-\alpha)]^k$
11	$\alpha^m(1-\alpha)^n[-\ln(1-\alpha)]^k$
12	$(1-\alpha)^n[1-\ln(1-\alpha)^{1/3}]^k$
13	$(1-\alpha)^n[1-\ln(1-\alpha)^{1/2}]^k$
14	$(1-\alpha)^n[(1-\alpha)^{-1/3}-1]^k$
15	$(1+\alpha)^n[(1+\alpha)^{1/3}-1]^k$

$$T_b=\frac{E_0-\sqrt{E_0^2-4E_0RT_{eo\text{ or }po}}}{2R} \qquad (9)$$

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.

Under static air conditions, the values of T_{po} and T_b obtained by Eqs.(**8**) and (**9**) using the values of T_p, β and E_0 in Table 4 are 306.28 ℃ and 322.74 ℃, respectively. These values approach the calculated values under the condition of flowing N_2 gas, indicating that under our experimental conditions, the atmosphere have not effect on the values of T_{po} and T_b of the title complex.

3 Conclusions

The mechanism of the thermal decomposition reaction of the title compound can be described by the scheme shown in text. The kinetic equations of the dehydration and exothermic decomposition processes can be expressed respectively as

$$\frac{d\alpha}{dT}10^{10.85}(1-\alpha)[-\ln(1-\alpha)]^{\frac{3}{4}}e^{-1.515\times10^4/T}$$

and

$$\frac{d\alpha}{dT}=10^{10.97}(1-\alpha)[-\ln(1-\alpha)]^{\frac{1}{2}}e^{-1.818\times10^4/T}$$

The apparent activation energy and pre-exponential constant of the major exothermic decomposition reaction of the compound are 178.5 kJ·mol^{-1} and $10^{13.01}$ s^{-1} for static air conditions, and 163.2 kJ·mol^{-1} and $10^{11.75}$ s^{-1} for flowing N_2 gas conditions, respectively. The corresponding critical temperatures of thermal explosion are 322.74 ℃ and 316.28 ℃, respectively.

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