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Determination of standard molar enthalpy of formation and kinetic study of the thermal dehydration for $Yb(NCS)_3 \cdot 3Gly \cdot H_2O$

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Abstract

The complex of ytterbium isothiocyanate with glycine has been synthesized. Its chemical formula was proved to be $Yb(NCS)_3 \cdot 3Gly \cdot H_2O$ (Gly = glycine). By means of a thermochemical cycle suggested in this paper, the standard molar enthalpy of formation for this complex has been determined using calorimetry. Kinetic analysis of the thermal dehydration of this complex has been achieved by use of TG–DTG and DSC curves recorded under comparable experimental conditions, kinetic parameters being obtained from analysis of the TG–DTG and DSC curves by integral and differential methods. The most probable mechanism function is suggested by comparison of the kinetic parameters. Mathematical expressions for the kinetic compensation effect are derived. The results show that the kinetic mechanism obtained from TG–DTG analysis is the same as that from DSC analysis.

INTRODUCTION

The rare earth (RE) elements are often used as spectroscopic probes in systems of biological importance [1,2]. Because RE^{3+} ions can substitute the Ca^{2+} ion, great interest has been aroused in the study of coordination chemistry of rare earth ions with aminoacids. Glycine is a typical α-aminoacid. Complexes of rare earth compounds with glycine have been reported [3–6]. In this paper, the complex $Yb(NCS)_3 \cdot 3Gly \cdot H_2O$ has been prepared, characterized and studied by thermochemistry and thermal analysis.

In this paper, we suggested the following thermochemical cycle for deriving the standard molar enthalpy of formation of the complex $Yb(NCS)_3 \cdot 3Gly \cdot H_2O$.

$$Yb(NCS)_3 \cdot 6H_2O(c) + 3Gly \cdot 600H_2O(aq) \xrightarrow{\Delta H_1} Yb(NCS)_3 \cdot 3Gly \cdot 606H_2O(aq) \qquad (1)$$

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$$\mathrm{Yb(NCS)_3 \cdot 3Gly \cdot H_2O(c) + 605H_2O(l) \xrightarrow{\Delta H_2} Yb(NCS)_3 \cdot 3Gly \cdot 606H_2O(aq)} \quad (2)$$

$$\mathrm{Gly(c) + 200H_2O(l) \xrightarrow{\Delta H_3} \tfrac{1}{3}(3Gly \cdot 600H_2O)(aq)} \quad (3)$$

eqn. (1) + 3eqn. (3) − eqn. (2) → eqn. (4)

$$\mathrm{Yb(NCS)_3 \cdot 6H_2O(c) + 3Gly(c) \xrightarrow{\Delta H_4} Yb(NCS)_3 \cdot 3Gly \cdot H_2O(c) + 5H_2O(l)} \quad (4)$$

$$\Delta H_4 = \Delta H_1 + 3\Delta H_3 - \Delta H_2$$

For the TG–DTG curve, we use Achar et al.'s differential equation [7] and the Coats–Redfern integral equation [8] to analyze the nonisothermal dehydration. The integral and differential equations are

$$\ln\left(\frac{g(\alpha)}{T^2}\right) = \ln\left(\frac{AR}{\beta E}\left(1 - \frac{2RT}{E}\right)\right) - \frac{E}{RT} \quad (5)$$

$$\ln\left(\frac{\mathrm{d}\alpha/\mathrm{d}T}{f(\alpha)}\right) = \ln\frac{A}{\beta} - \frac{E}{RT} \quad (6)$$

For the DSC curve, we use Bagchi and Sen's integral and differential equations [9] to analyze the nonisothermal dehydration. The integral and differential equations are

$$\ln\left(\frac{g(\alpha)}{T - T_0}\right) = \ln\frac{A}{\beta} - \frac{E}{RT} \quad (7)$$

$$\ln\left\{\frac{\mathrm{d}\alpha/\mathrm{d}T}{f(\alpha)\left[E(T - T_0)/RT^2 + 1\right]}\right\} = \ln\frac{A}{\beta} - \frac{E}{RT} \quad (8)$$

In the above equations, α is the fraction of the reacted material, T is the absolute temperature, $f(\alpha)$ and $g(\alpha)$ are differential and integral mechanism functions respectively, E and A are the derived apparent activation energy and pre-exponential factor, respectively, R is the gas constant and β is the linear heating rate.

EXPERIMENTAL

Purification of reagents and preparation of the complex

Glycine was purified by means of recrystallization. The purified glycine was kept in a desiccator containing $CaCl_2$ until its mass became constant.

The complex $Yb(NCS)_3 \cdot 6H_2O$ was prepared as previously described [10].

To prepare $Yb(NCS)_3 \cdot 3Gly \cdot H_2O$, $Yb(NCS)_3 \cdot 6H_2O$ and glycine (in molar ratio 1:3) were dissolved in distilled water, and condensed at a constant temperature of 50–55°C. At last, the solution became sticky, then the solvent was changed by adding anhydrous alcohol. Upon adding isopropanol dropwise, a gelatinous precipitate appeared which after a few days solidified. The solid was filtered off and washed with anhydrous alcohol and dried over phosphorus pentoxide until its mass became constant. The resulting complex was $Yb(NCS)_3 \cdot 3Gly \cdot H_2O$.

Component analysis of the complex

The Yb^{3+} content in the complex was determined by EDTA titration, and the NCS^- content was determined by Volhard's method. The content of C, H and N in the complex were determined using a Perkin Elmer 240C elemental analyser (USA).

Physical measurements

The IR spectrum of the complex was recorded using a Nicolet Model 20SX spectrophotometer. The sample was mounted as a mull in a KBr disc and examined between 4000 and 300 cm^{-1}.

The X-ray powder diffractogram of the complex was obtained with an X-ray diffractometer (D/Hax-rA, Rigaku, Japan) with copper radiation and a nickel filter.

Calorimeter and calorimetric experiments

A modified RD-I heat conducting automatic calorimeter (The Scientific Instruments Factory of Sichuan University, People's Republic of China) was used for the calorimetric measurements. It has 144 pairs of thermocouples. Heat changes up to 2 J could be measured exactly. Details of the apparatus, principles and calorimetry of the calorimeter have been published elsewhere [10,11].

The reliability of the calorimetric system was monitored in the present experiments by measuring the integral heat of solution of 1 mol KCl (Merck) in 200 mol H_2O at 298.15 K. The measured value is 17.64 ± 0.07 kJ mol^{-1}, which is consistent with the literature value of 17.524 ± 0.028 kJ mol^{-1} [12].

According to the thermochemical cycle mentioned above, we measured the integral heats of solution of $Yb(NCS)_3 \cdot 6H_2O$ in aqueous glycine solution (ΔH_1), of $Yb(NCS)_3 \cdot 3Gly \cdot H_2O$ in water (ΔH_2) and of glycine in water (ΔH_3). Each measurement was repeated nine times.

TG–DTG experimental equipment and conditions

Thermogravimetric analysis of finely-powdered sample was performed on a Perkin Elmer Model TGS-2, with a nitrogen flow rate of 20 ml min^{-1}, in the temperature range 40–900°C and with the linear heating rate of 5.00°C min^{-1}. The amount of sample used was 2.7895 mg.

DSC experimental equipment and conditions

Differential scanning calorimetry (DSC) was done using a Perkin Elmer Model DSC-2C at a scanning rate of 5.00°C min^{-1} with a nitrogen flow rate of 20 ml min^{-1}. The amount of sample used was 3.79 mg.

The reliability of the temperature and the calorimetric systems was monitored in the present experiment by measuring the melting point and the heat of fusion of indium under nitrogen atmosphere (20 ml min^{-1}) at a heating rate of 5.00°C min^{-1}. The measured values are 429.5 K and 3.29 kJ mol^{-1}, which are consistent with the literature values of 430 K and 3.26 kJ mol^{-1} [13].

RESULTS AND DISCUSSION

Component analysis of the complex

The results of component analysis of the complex are (%): Yb^{3+}, 29.11 (29.30); NCS^-, 29.44 (29.51); C, 18.49 (18.31); H, 2.82 (2.90); N, 14.43 (14.23). The values in parentheses are calculated values. The chemical formula of the complex is $Yb(NCS)_3 \cdot 3Gly \cdot H_2O$.

Yin et al. [4] synthesized $RE(NCS)_3 \cdot 3Gly \cdot H_2O$ (RE = La, Ce, Pr, Nd). It is difficult to prepare the complexes of heavy rare earth isothiocyanates with glycine using the method described in the literature [4]. In this paper, we used the method of changing solvent to synthesize the complex of ytterbium isothiocyanate with glycine.

Physical measurements

The IR wavenumbers of some group vibrations in the complex are listed in Table 1.

If we compare the frequencies of some group vibrations of glycine in free and complexed forms, the results indicate that glycine retains its zwitterionic structure in its ytterbium complex. This excludes the possibility of coordination of nitrogen to the ytterbium ion.

The O–H asymmetric stretch and symmetric stretch of water molecule in $Yb(NCS)_3 \cdot 3Gly \cdot H_2O$ have been observed at 3540 and 3380 cm^{-1}, respectively. This shows that the water molecule in the complex is hydrogen bonded. Lower shifts (83 cm^{-1}) of $-NH_3^+$ stretch in complexed glycine may be due to the formation of hydrogen bonds between glycine and water in the complex [6].

TABLE 1

Wavenumbers (cm^{-1}) of some group vibrations in $Yb(NCS)_3 \cdot 3Gly \cdot H_2O$

Approximate description of mode	Gly [14]	$Yb(NCS)_3 \cdot 3Gly \cdot H_2O$ [a]
Vibrations of NH_3^+ group of glycine		
Stretch	3170	3110s, 3087s
Asymmetric bend	1585	1623s
Symmetric bend	1492	1498m
Rock	1131, 1110	1111m, 1098m
Vibrations of COO^- group of glycine		
Asymmetric stretch	1610	1602s
Symmetric stretch	1413	1408s
Bend	693	669w, 700w
Vibrations of CH_2 group of glycine		
Bend	1445	1446s
Wag	1333	1326s
Rock	910	909m
Skeletal vibration of glycine		
$C-N^+$ stretch	1033	1026w
C–C stretch	890	752w
Vibrations of OH group of water molecule		
Asymmetric stretch		3538s
Symmetric stretch		3379s
Vibrations of NCS^- group		
Stretch of C–N		2066s
Bend		475w

[a] Intensity of peaks: s, strong; m, medium; w, weak.

In free glycine, the $\Delta\nu(COO^-) = \nu_{as}(COO^-) - \nu_s(COO^-) = 197\ cm^{-1}$. In complexed glycine, the $\Delta\nu(COO^-)$ is 194 cm^{-1}. This indicates that in the complex, the two oxygen of $-COO^-$ have higher symmetry, and the two oxygen coordinated with Yb^{3+} ion.

The frequencies of 2066 and 475 cm^{-1} prove that in the complex NCS^- groups are coordinated through nitrogen to Yb^{3+} ion.

Comparing the X-ray diffraction data of $Yb(NCS)_3 \cdot 3Gly \cdot H_2O$ $Yb(NCS)_3 \cdot 6H_2O$ and glycine, we can conclude that the three compounds belong to different phases and the prepared complex is a new substance.

Results of calorimetric experiments

The experimental data of integral heats ΔH_1, ΔH_2, ΔH_3 in the thermochemical cycle mentioned above and the calculated total heat of reaction ΔH_4 are 16.25 ± 0.12 kJ mol^{-1}, 28.30 ± 0.17 kJ mol^{-1}, 14.49 ± 0.04 kJ mol^{-1} and 31.42 kJ mol^{-1}, respectively.

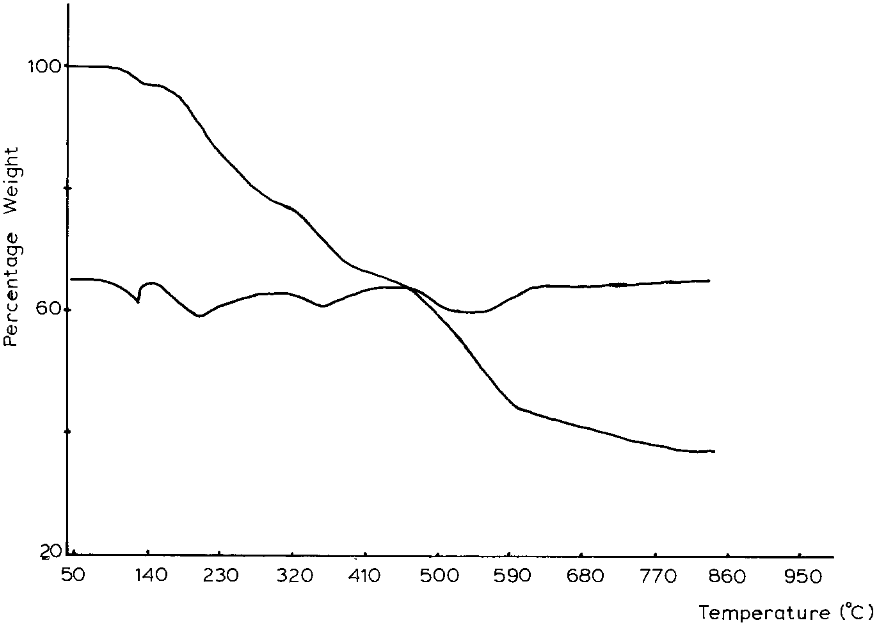

Fig. 1. The TG–DTG curve of $Yb(NCS)_3 \cdot 3Gly \cdot H_2O$.

The calculation of standard molar enthalpy of formation of $Yb(NCS)_3 \cdot 3Gly \cdot H_2O$ is shown below:

$$\Delta H_f^{\ominus} Yb(NCS)_3 \cdot 3Gly \cdot H_2O(c) = \Delta H_4 + \Delta H_f^{\ominus} Yb(NCS)_3 \cdot 6H_2O(c) - 5\Delta H_f^{\ominus} H_2O(l) + 3\Delta H_f^{\ominus} Gly(c)$$

$\Delta H_f^{\ominus} Yb(NCS)_3 \cdot 6H_2O(c) = -2167.8$ kJ mol^{-1} (see ref. 10)

$\Delta H_f^{\ominus} Gly(c) = -528.5$ kJ mol^{-1} (see ref. 15)

$\Delta H_f^{\ominus} H_2O(l) = -285.83$ kJ mol^{-1} (see ref. 16)

The result of the calculation is $\Delta H_f^{\ominus} Yb(NCS)_3 \cdot 3Gly \cdot H_2O(c) = -2292.7$ kJ mol^{-1} (298.15 K).

Nonisothermal analysis

Thermal decomposition process

The TG–DTG and DSC curves of $Yb(NCS)_3 \cdot 3Gly \cdot H_2O$ are shown in Figs. 1 and 2.

According to the TG–DTG curve, we concluded that the probable thermal decomposition steps of $Yb(NCS)_3 \cdot 3Gly \cdot H_2O$ are as shown in Table 2. There is a peak between 358 and 403 K in the DSC curve. The temperature range of 358–403 K (85–130°C) is consistent with the temperature range of the dehydration process in the TG–DTG curve. This peak is

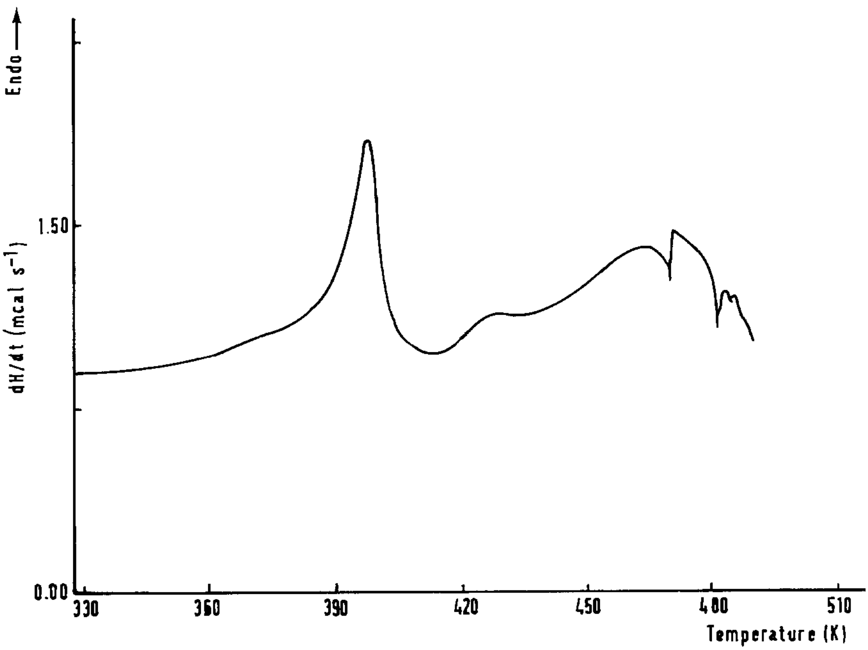

Fig. 2. The DSC curve of $Yb(NCS)_3 \cdot 3Gly \cdot H_2O$.

considered as the endothermic peak of the dehydration process of $Yb(NCS)_3 \cdot 3Gly \cdot H_2O$. With treatment of the area of this peak, we found the dehydration enthalpy change to be 98.82 kJ mol^{-1}.

Kinetic study for the dehydration process

TG–DTG curve. The possible forms of $g(\alpha)$ and $f(\alpha)$ are listed in Table 3. The original data for the dehydration process of this complex determined by TG–DTG curve are listed in Table 4.

Using the possible forms of $g(\alpha)$ and $f(\alpha)$, the data in Table 4 are analysed by use of eqns. (5) and (6). For eqns. (5) and (6), the kinetic

TABLE 2

Thermal decomposition of $Yb(NCS)_3 \cdot 3Gly \cdot H_2O$

Step	Decomposition process	Mass loss(%)
1	$Yb(NCS)_3 \cdot 3Gly \cdot H_2O \xrightarrow{85-149°C} Yb(NCS)_3 \cdot 3Gly$	3.05 (3.05) [a]
2	$Yb(NCS)_3 \cdot 3Gly \xrightarrow{149-296°C} Yb(NCS)_3 \cdot 1.5Gly$	19.51 (19.67) [a]
3	$Yb(NCS)_3 \cdot 1.5Gly \xrightarrow{296-436°C} Yb(NCS)_3 \cdot 0.5Gly$	15.97 (16.32) [a]
4	$Yb(NCS)_3 \cdot 0.5Gly \xrightarrow{436-840°C} Yb_2S_3$	42.89 (42.54) [a]

[a] Values in parentheses are calculated values.

TABLE 3

Several kinetic functions used for the present analysis

Function no.	Function form	
	Differential form $f(\alpha)$	Integral form $g(\alpha)$
1	$1/2\alpha$	α^2
2	$[-\ln(1-\alpha)]^{-1}$	$\alpha+(1-\alpha)\ln(1-\alpha)$
3	$3[(1-\alpha)^{-1/3}-1]^{-1}/2$	$(1-2\alpha/3)-(1-\alpha)^{2/3}$
4	$3(1-\alpha)^{2/3}[1-(1-\alpha)^{1/3}]^{-1}/2$	$[1-(1-\alpha)^{1/3}]^2$
5	$3(1+\alpha)^{2/3}[(1+\alpha)^{1/3}-1]^{-1}/2$	$[(1+\alpha)^{1/3}-1]^2$
6	$3(1-\alpha)^{4/3}[\{1/(1-\alpha)^{1/3}-1\}]^{-1}/2$	$[1/(1-\alpha)^{1/3}-1]^2$
7	$(1-\alpha)$	$-\ln(1-\alpha)$
8	$3(1-\alpha)[-\ln(1-\alpha)]^{1/3}/2$	$[-\ln(1-\alpha)^{2/3}$
9	$2(1-\alpha)[-\ln(1-\alpha)]^{1/2}$	$[-\ln(1-\alpha)]^{1/2}$
10	$3(1-\alpha)[-\ln(1-\alpha)]^{2/3}$	$[-\ln(1-\alpha)]^{1/3}$
11	$4(1-\alpha)[-\ln(1-\alpha)]^{3/4}$	$[-\ln(1-\alpha)]^{1/4}$
12	$2(1-\alpha)^{1/2}$	$1-(1-\alpha)^{1/2}$
13	$3(1-\alpha)^{2/3}$	$1-(1-\alpha)^{1/3}$
14	1	α
15	$2\alpha^{1/2}$	$\alpha^{1/2}$
16	$3\alpha^{2/3}$	$\alpha^{1/3}$
17	$4\alpha^{3/4}$	$\alpha^{1/4}$
18	$(1-\alpha)^2$	$(1-\alpha)^{-1}-1$
19	$2(1-\alpha)^{3/2}$	$(1-\alpha)^{-1/2}$

analyses are completed by the linear least squares method on an IBM computer. The T term in the right hand side of eqn. (5) adopted $\bar{T}$, the mean temperature of the original data. The results are shown in Table 5.

The results in Table 5 clearly show that the values of E and A from the two methods are approximately the same and the linear correlation coefficients are better when the probable mechanism function is logically func-

TABLE 4

Data for the dehydration process of $Yb(NCS)_3 \cdot 3Gly \cdot H_2O$ determined by TG–DTG

No.	T_i (K)	α_i	$[d\alpha/dT]_i$ (K^{-1})
1	383.15	0.2393	0.0758
2	388.15	0.3574	0.1024
3	393.15	0.4820	0.1404
4	398.15	0.5967	0.1888
5	399.15	0.6590	0.2000
6	400.15	0.7082	0.2094
7	401.15	0.7508	0.1790
8	402.15	0.8033	0.1442
9	403.15	0.8328	0.1224
10	404.15	0.8689	0.0996

TABLE 5

Results of analysis of the thermal dehydration data of $Yb(NCS)_3 \cdot 3Gly \cdot H_2O$ in Table 4 by integral eqn. (5) and differential eqn. (6) methods

No.	Integral method			Differential method		
	ln A (s^{-1})	E (kJ mol^{-1})	r	ln A (s^{-1})	E (kJ mol^{-1})	r
1	39.31	148.52	0.9971	29.79	112.54	0.9021
2	45.91	171.17	0.9974	42.21	154.18	0.9675
3	47.47	180.76	0.9969	46.26	171.84	0.9813
4	53.72	200.29	0.9953	56.75	205.22	0.9936
5	31.07	130.11	0.9963	19.23	86.54	0.8396
6	75.00	267.10	0.9864	88.23	305.40	0.9948
7	29.21	112.61	0.9911	37.63	135.20	0.9903
8	16.77	72.88	0.9906	25.20	95.48	0.9753
9	10.49	53.03	0.9900	18.91	75.62	0.9558
10	4.10	33.18	0.9887	12.49	55.76	0.9121
11	0.85	23.26	0.9871	9.20	45.83	0.8697
12	21.10	89.72	0.9963	21.20	85.11	0.9285
13	23.02	96.91	0.9950	26.04	101.80	0.9636
14	15.67	71.01	0.9968	6.15	35.02	0.5522
15	3.53	32.22	0.9961	−6.02	−3.75	−0.0710
16	−0.62	19.30	0.9952	−10.25	−16.66	−0.3022
17	−2.64	12.83	0.9939	−12.45	−23.13	−0.4028
18	47.97	171.15	0.9731	69.11	235.37	0.9887
19	8.04	43.56	0.9054	52.68	185.28	0.9943

tion no. 4. We concluded that the probable mechanism function of dehydration process of the complex $Yb(NCS)_3 \cdot 3Gly \cdot H_2O$ is the function no. 4 in Table 3. The kinetic equation of this process is

$$\mathrm{d}\alpha/\mathrm{d}T=\frac{A}{\beta}\exp\left(-\frac{E}{RT}\right)\frac{3}{2}(1-\alpha)^{2/3}\left[1-(1-\alpha)^{1/3}\right]^{-1}$$

DSC curve. The original data for the dehydration process (peak 1) of $Yb(NCS)_3 \cdot 3Gly \cdot H_2O$ detemined from the DSC curve are listed in Table 6.

The data are fitted to eqn. (7) by the linear least-squares method on a TI-59 computer.

Equation (8) may be solved by the iterative method on a computer. A value of E may be assumed for the term E in the left hand of eqn. (8), and E is greater than 0. Using the E value and $f(\alpha)$ in Table 3, the original data in Table 6 are analyzed by use of eqn. (8) and the modified E value may be obtained by the linear least squares method. This modified value of E is used as a starting value for the next iteration, which yields another modified value of E. Thus, after a few iterations, consistent values of E and A may be obtained. The results are listed in Table 7.

TABLE 6

Data for the dehydration process of $Yb(NCS)_3 \cdot 3Gly \cdot H_2O$ determined by DSC (Peak I) [a]

No.	T_i (K)	α_i	$[(d\alpha/dT)]_i$ (K^{-1})
1	368.00	0.0260	0.00561
2	373.00	0.0605	0.00801
3	378.00	0.1080	0.01042
4	383.00	0.1716	0.01475
5	388.00	0.2620	0.02132
6	393.00	0.4101	0.03847
7	398.00	0.7000	0.07630
8	403.00	0.9491	0.01924

[a] $T_0 = 358.00$ K, $H_0 = 582.92$ mJ, $\beta = 5.00$°C min^{-1}.

From Table 7 we drew the same conclusion on the kinetic mechanism of the dehydration process of $Yb(NCS)_3 \cdot 3Gly \cdot H_2O$ as we obtained from Table 5.

TABLE 7

Results of analysis of the thermal dehydration data of $Yb(NCS)_3 \cdot 3Gly \cdot H_2O$ in Table 6 by integral (eqn. (7)) and differential (eqn. (8)) methods

No.	Integral method			Differential method			
	ln A (s^{-1})	E (kJ mol^{-1})	r	E_0 [a] (kJ mol^{-1})	ln A (s^{-1})	E (kJ mol^{-1})	r
1	52.02	195.29	0.9966	195.29	40.91	160.09	0.9556
2	56.79	212.25	0.9974	212.25	50.27	191.58	0.9824
3	58.16	221.17	0.9978	221.17	53.22	205.56	0.9875
4	62.49	234.69	0.9946	234.69	61.59	231.82	0.9879
				231.82	61.63	231.92	0.9879
5	44.68	179.38	0.9946	179.38	31.59	137.94	0.9341
6	79.61	288.06	0.9772				
7	25.52	104.26	0.9758				
8	8.80	22.49	0.9465				
9	1.94	26.61	0.8659				
10	−2.27	0.74	0.0567				
11	−9.84	−12.20	−0.7136				
12	19.06	86.31	0.9917	86.31	18.43	84.36	0.9374
13	20.43	91.81	0.9876	91.81	22.07	97.09	0.9485
14	15.19	72.10	0.9976	72.10	6.97	46.18	0.7114
15	−3.22	10.54	0.8991				
16	−9.34	−9.95	−0.8483				
17	−12.42	−20.25	−0.9435				
18	40.86	152.15	0.9244				
19	−8.07	−11.03	−0.2741				

[a] E_0 is the assumed E value.

TABLE 8

Calculated values of kinetic parameters of thermal dehydration for $Yb(NCS)_3 \cdot 3Gly \cdot H_2O$

	TG–DTG ($\alpha = 0.2393$–0.8689)		DSC ($\alpha = 0.0260$–0.9491)	
	Integral	Differential	Integral	Differential
E (kJ mol^{-1})	200.29	205.22	234.69	231.92
ln A (s^{-1})	53.72	56.75	62.49	61.63
ΔS (J K^{-1} mol^{-1})	298.86	324.05	371.82	364.67
r	0.9953	0.9936	0.9946	0.9879

Using the value of A, we calculated the activation entropy ΔS

$$\Delta S = R \ln \frac{hA}{K_b T_s}$$

In this equation, R is the gas constant, h is Planck's constant, K_b is Boltzmann's constant, T_s is the temperature of the top of the peak. For the DTG peak T_s is 400 K and for the DSC peak T_s is 398 K.

The calculated values of kinetic parameters of dehydration process of $Yb(NCS)_3 \cdot 3Gly \cdot H_2O$ are listed in Table 8.

The kinetic compensation effect

According to the mathematical expression for the kinetic compensation effect, $\ln A = aE + b$, we fitted the obtained kinetic parameters (E and ln A) from the integral and differential methods (for TG–DTG) and from the integral method (for DSC) (see Tables 5 and 7) by the linear least-squares method on a TI-59 computer, and obtained the kinetic compensation parameters a and b. The values of a and b are given in Table 9. The results indicate that the kinetic parameters ln A and E may be connected through a and b.

From the results in Table 8, we can see that although the kinetic parameters obtained from TG–DTG analysis are comparable with those obtained from DSC analysis, the differences between them are obvious. However from the results in Table 9, the kinetic compensation parameters a and b obtained from TG–DTG analysis are consistent with those obtained from DSC analysis. This result shows that the kinetic compensa-

TABLE 9

Calculated values of kinetic compensation parameters for $Yb(NCS)_3 \cdot 3Gly \cdot H_2O$

Method	a	b	r
TG–DTG	0.3055	−5.5613	0.9987
DSC	0.2927	−5.7073	0.9991

tion parameters may be characteristic of the decomposition reaction itself. It is more reasonable to describe the thermal decomposition reaction using kinetic compensation parameters than using the kinetic parameters or the temperature of decomposition.

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