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STUDIES ON NON-ISOTHERMAL KINETICS OF THE THERMAL DECOMPOSITION OF $Eu_2(BA)_6(bipy)_2$

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Abstract

The thermal decomposition of $Eu_2(BA)_6(bipy)_2$ ($BA=C_2H_5O_2^-$, benzoate; $bipy=C_{10}H_8N_2$, 2,2'- bipyridine) and its kinetics were studied under the non-isothermal condition by TG-DTG, IR and SEM methods. The kinetic parameters were obtained from analysis of the TG-DTG curves by the Achar method, the Madhusudanan–Krishnan–Ninan (MKN) method, the Ozawa method and the Kissinger method. The most probable mechanism function was suggested by comparing the kinetic parameters. The kinetic equation for the first stage can be expressed as: $d\alpha/dt = A\exp(-E/RT)3(1-\alpha)^{2/3}$.

Keywords: benzoic acid, europium complex, kinetics, non-isothermal, thermal decomposition

Introduction

The complexes formed by rare earth and aromatic carboxylic acid have many special structures and interesting luminous properties, thus arouse people's interest to study them. They can be used in many areas such as extraction and separation, germicide, catalyst, luminous materials and functional materials and so on. In this paper, based on the preparation and determination of the crystal structure and luminescence spectrum of the $Eu_2(BA)_6(bipy)_2$ [1], we discussed its thermal decomposition behaviour procedure by TG-DTG, IR and SEM techniques and the corresponding non-isothermal kinetics by means of the Achar method [2], the MKN method [3], the Ozawa method [4] and the Kissinger method [5], respectively.

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Experimental

Sample

The $Eu_2(BA)_6(bipy)_2$ was prepared as described previously [1].

TG and DTG analysis

The TG and DTG experiments for the title compounds were performed using a Perkin Elmer's TGA7 thermogravimetric analyzer under a nitrogen atmosphere, at a flow rate of 40 ml min^{-1}. The heating rates used were 3, 5, 7, 10°C min^{-1} from ambient to 925°C and the sample size was 2.2±0.2 mg.

Electron microscopic observations

Small quantity of the sample was dispersed regularly on the sample holder and Au was sprayed for 5 min with Hitachi IB-5. Then, it was observed by the Hitachi S-570 scanning electron microscope.

Infrared spectroscopic analysis

Infrared spectroscopic analyses were recorded for KBr discs on Bio-Rad FTS-135 spectrometer, between 4000 and 400 cm^{-1}.

Results and discussion

Thermogravimetric decomposition data

TG and DTG curves of $Eu_2(BA)_6(bipy)_2$ are shown in Fig. 1. The IR spectra of some intermediate products of the thermal decomposition are shown in Fig. 2. The results of

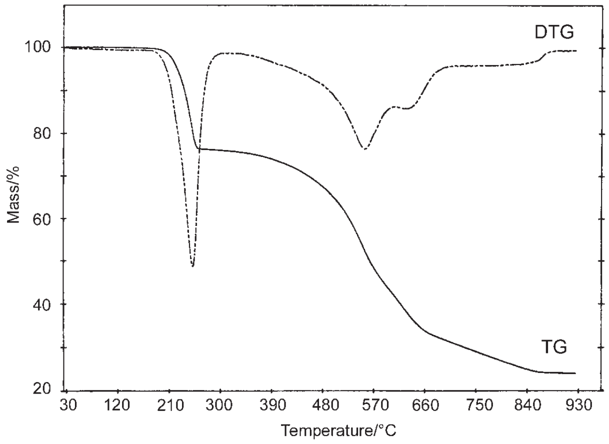

Fig. 1 TG-DTG curves of $Eu_2(BA)_6(bipy)_2$ using a heating rate of 3°C min^{-1}

thermal analysis indicate that the thermal decomposition of $Eu_2(BA)_6(bipy)_2$ begins at 171 and ends at 753°C. The thermal decomposition process of $Eu_2(BA)_6(bipy)_2$ can be divided into four stages, as was observed by the DTG curve (Fig. 1), and there are mass loss with maximum rate at 241, 524 and 601°C in the DTG curve. In the first stage, be-

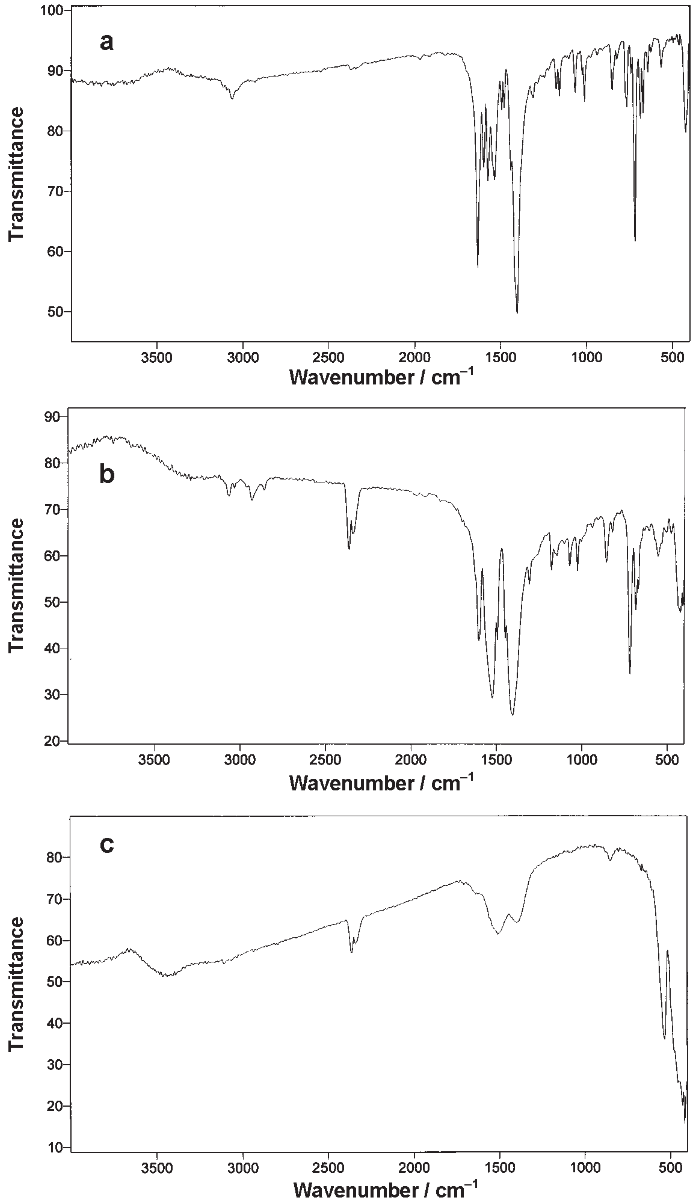

Fig. 2 IR spectra of $Eu_2(BA)_6(bipy)_2$ at a – RT; b – 292°C and c – 753°C

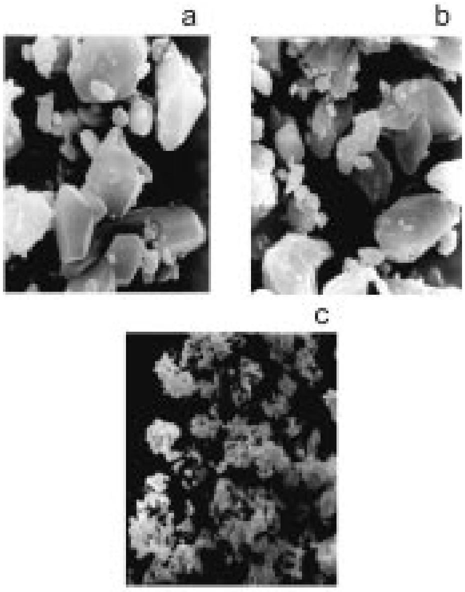

Fig. 3 SEM pictures of $Eu_2(BA)_6(bipy)_2$ at a – RT; b – 292°C and c – 753°C

tween 171 and 292°C, a mass loss of 23.89% was observed corresponding to the loss of the 2 mol $C_{10}H_8N_2$ (theoretical mass loss is 23.26%) and the formation of $Eu_2(BA)_6$ from $Eu_2(BA)_6(bipy)_2$. The degradation can also be confirmed by the bond distances in Table 1. Eu–N distance is longer than other bond distance; theoretically, this bond is less stable and easy to be broken down.

The IR spectrum of the complex at 292°C shows that the finger mark region changed (compared with Fig. 2(a)). From the SEM pictures, the apparent form of the complex changed from a smooth-surface crystal to a crackled crystal (Fig. 3). In the second-stage, $Eu_2(BA)_6$ is decomposed at 292–581°C with the mass loss of 35.9%. The theoretical mass loss is 36.07% corresponding to the loss of 4 mol BA and the formation of $Eu_2(BA)_2$. The process can also be explained by structural data in Table 1. From Table 1,

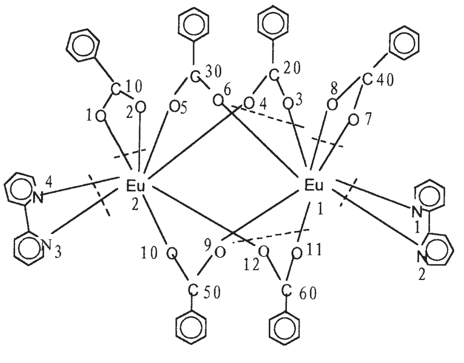

Fig. 4 Molecular structure of of $Eu_2(BA)_6(bipy)_2$

the average bond lengths of Eu–O in 1, 3, 5, 6 are longer than those in 2, 4. Thus the bonds of Eu–O in 1, 3, 5, 6 can be broken down and the group of BA can be simultaneously lost more easily, as indicated by the broken line in Fig. 4.

Table 1 Main bond lengths/nm, according to [1]

Serial number of BA	Bond lengths of Eu–O(N)				Average bond lengths
1	Eu(1)–O(3)	2.366	Eu(2)–O(4)	2.321	2.344
2	Eu(1)–O(6)	2.297	Eu(2)–O(5)	2.333	2.315
3	Eu(1)–O(11)	2.310	Eu(2)–O(12)	2.369	2.340
4	Eu(1)–O(9)	2.328	Eu(2)–O(10)	2.328	2.328
5	Eu(1)–O(7)	2.483	Eu(1)–O(8)	2.398	2.441
6	Eu(2)–O(1)	2.446	Eu(2)–O(2)	2.477	2.462
–	Eu(1)–N(1)	2.651	Eu(1)–N(2)	2.593	2.622
–	Eu(2)–N(3)	2.578	Eu(2)–N(4)	2.641	2.610

The TG curve shows the third stage began at 581 and completed at 659°C accompanied by 10.12% mass loss. It is in agreement with the theoretical value of the mass loss of 9.80%, corresponding to the loss of 1.5 mol C_6H_5, and the formation of $Eu_2(BA)_{0.5}(COO)_{1.5}$. In the fourth stage, the experimental value for the mass loss of 5.29% found between 659 and 753°C in the TG curve is in agreement with the theoretical mass loss is 5.85%, corresponding to the loss $C_5H_{2.5}O$ and formation of Eu_2O_3. As shown in Fig. 2, the IR spectrum of product of thermal decomposition up to 753°C is much different from that the complex $Eu_2(BA)_6(bipy)_2$. The IR bands of the ligands are almost lost, the rest small peaks are for Eu_2O_3 bands (the characteristic absorption peak in 1633 cm^{-1} for C=O group of the title complex heated at 753°C disappeared). The apparent form of SEM pictures for the product at 753°C is also completely different from that of the complex at room temperature. The formation of above-mentioned products from $Eu_2(BA)_6(bipy)_2$ should be accomplished with a theoretical overall mass loss of 74.99%. It was in agreement with the experimental value of 75.28%. From the above analysis, the thermal decomposition process of $Eu_2(BA)_6(bipy)_2$ may be expressed by the following scheme:

$$Eu_2(BA)_6(bipy)_2 \rightarrow Eu_2(BA)_6 \rightarrow Eu_2(BA)_2 \rightarrow Eu_2(BA)_{0.5}(COO)_{1.5} \rightarrow Eu_2O_3$$

Non-isothermal decomposition kinetics

In the present work, the Achar method, the MKN method, the Ozawa method and the Kissinger method were applied to study the kinetics of the first decomposition processes of $Eu_2(BA)_6(bipy)_2$. The differential, integral, Ozawa and Kissinger equations are as follows

$$\ln\left[\frac{\mathrm{d}\alpha/\mathrm{d}t}{f(\alpha)}\right]=\ln A-\frac{E}{RT} \qquad \left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}=\beta\frac{\mathrm{d}\alpha}{\mathrm{d}T}\right) \tag{1}$$

$$\ln\left[\frac{g(\alpha)}{T^{1.9215}}\right]=\ln\frac{AE}{\beta R}+3.7721-1.9215\ln E-0.12039\frac{E}{T} \tag{2}$$

$$\lg\beta+\frac{0.4567E}{RT}=C \tag{3}$$

$$\frac{\mathrm{d}\ln\frac{\beta}{T_\mathrm{P}^2}}{\mathrm{d}\frac{1}{T_\mathrm{P}}}=-\frac{E}{R} \tag{4}$$

where α is the fraction of conversion, $\mathrm{d}\alpha/\mathrm{d}t$ is the rate of conversion, T is the absolute temperature, T_P is the peak temperature, A is the pre-exponential factor, R is the gas constant, E is the apparent activation energy, β is the linear heating rate, $f(\alpha)$ and $g(\alpha)$ are the differential and integral mechanism function, respectively, C is a constant.

The free energy of activation (ΔG) can be calculated using the following equations [6]

$$k(T)=A\exp\left(-\frac{E}{RT}\right) \tag{5}$$

$$k(T)=\nu\exp\left(-\frac{\Delta G}{RT}\right) \tag{6}$$

Substituting (6) into (5), leads to

$$A\exp\left(-\frac{E}{RT}\right)=\nu\exp\left(-\frac{\Delta G}{RT}\right) \tag{7}$$

where $k(T)$ is the rate constant as a function of temperature, ν is the Einstein vibration frequency.

The value of α, T and $\mathrm{d}\alpha/\mathrm{d}T$ obtained by the TG-DTG curves (Fig. 1) are listed in Table 2. By substituting value in Table 2 and the 30 different mechanism functions $f(\alpha)$ and $g(\alpha)$ in reviews [7–8] into Eqs (1) and (2), the kinetic parameters E, $\ln A$ and linear correlation coefficients r were obtained by the linear least squares method, and listed in Table 3.

The values of E corresponding to the value of α for the first-stage decomposition reaction obtained by the Ozawa method are shown in Table 4. It is clear that the value of E is nearly constant, which indicates that the mechanism of the first-stage decomposition reaction is constant. By the Kissinger method we also obtained the following results: E_K=116.6 kJ mol^{-1}, r=0.9952. If all the following conditions are satisfactory at the same time: (1) the values of E and $\ln A$ obtained by the differential and integral methods are approximately equal; (2) the linear correlation coefficient is better; (3) the values of E and $\ln A$ accord with the universal law (the value of E ranges from 80 to 250 kJ mol^{-1}, $\ln A$ from 16.91 to 69.09 s^{-1}) [9]; (4) the values of E obtained by the Ozawa method and the Kissinger method are also approximately identical with those obtained by Achar method and MKN method mentioned above, the relevant function under such conditions is the probable mechanism function of thermal decomposition of the complex.

By comparing the *E*, ln*A* and *r* in Table 3 obtained by Achar method and MKN method, we can see that only the values obtained when the function No is 13 can satisfy the four above-mentioned conditions at the same time. So the probable mechanism func-

Table 2 Base data for the first-stage decomposition reaction of $Eu_2(BA)_6(bipy)_2$ determined by TG and DTG (β=3°C min^{-1})

No	*T*/K	α	dα/d*T*	No.	*T*/K	α	dα/d*T*
1	468.14	0.0324	0.165	11	506.09	0.5754	1.59
2	472.35	0.0496	0.234	12	510.03	0.6899	1.751
3	476.57	0.074	0.329	13	514.52	0.8067	1.83
4	480.78	0.1082	0.455	14	518.73	0.9049	1.698
5	485.00	0.1538	0.616	15	522.94	0.9597	1.307
6	489.21	0.2130	0.803	16	527.16	0.9778	0.873
7	493.43	0.2855	1.009	17	531.38	0.9825	0.554
8	497.64	0.3714	1.216	18	535.64	0.9847	0.355
9	501.86	0.4689	1.412	19	538.45	0.9859	0.267
10	503.28	0.5035	1.474				

Table 3 Results of the kinetic analysis of $Eu_2(BA)_6(bipy)_2$. Stage I(β=3°C min^{-1})

Function No.	Achar method			MKN method		
	E/kJ mol^{-1}	ln(*A*/s^{-1})	*r*	*E*/kJ mol^{-1}	ln(*A*/s^{-1})	*r*
1	128.14	31.53	0.7864	196.14	43.98	0.9515
2	178.17	43.37	0.9006	218.99	49.14	0.9657
3	204.20	48.36	0.9370	230.15	50.48	0.9720
4	251.24	60.11	0.9713	254.18	56.58	0.9823
5	103.95	23.14	0.7239	179.13	37.35	0.9436
6	392.35	95.35	0.9901	348.27	80.37	0.9965
7	167.17	42.70	0.9789	144.09	32.85	0.9921
8	116.47	30.33	0.9671	93.38	20.48	0.9916
9	91.12	24.06	0.9538	68.03	14.21	0.9910
10	65.77	17.66	0.9250	42.68	7.79	0.9897
11	53.09	14.38	0.8963	30.01	4.48	0.9884
12	96.62	24.39	0.9071	114.37	24.51	0.9736
13	120.14	29.86	0.9511	123.07	26.36	0.9811
14	26.06	7.46	0.3517	94.05	19.92	0.9473
15	–24.98	–4.92	0.4208	43.02	7.52	0.9374

Table 3 Continued

Function No.	Achar method			MKN method		
	E/kJ mol^{-1}	$\ln(A/s^{-1})$	r	E/kJ mol^{-1}	$\ln(A/s^{-1})$	r
16	–42.00	–9.22	0.6528	26.00	3.16	0.9245
17	–50.50	–11.45	0.7380	17.49	0.8444	0.9080
18	308.29	77.94	0.9715	235.17	56.01	0.9880
19	237.73	59.63	0.9791	62.53	13.79	0.9928
20	77.10	19.56	0.6719	60.03	11.72	0.8426
21	319.28	79.30	0.9880	296.20	69.43	0.9926
22	471.40	115.62	0.9902	448.31	105.71	0.9927
23	623.51	151.81	0.9911	600.42	141.89	0.9928
24	449.41	113.87	0.9579	274.20	68.01	0.9078
25	131.90	32.51	0.9630	127.87	27.30	0.9844
26	–115.06	–27.08	0.6678	69.68	14.17	0.8960
27	–256.17	–61.91	0.8031	55.36	10.70	0.8532
28	–397.29	–96.86	0.8438	45.62	8.29	0.8167
29	54.58	14.39	0.8846	57.53	10.88	0.9782
30	71.10	17.85	0.8815	53.17	9.92	0.9692

tion in the first stage of decomposition of the title compound is function No. 13 ($f(\alpha)=3(1-\alpha)^{2/3}$, $g(\alpha)=1-(1-\alpha)^{1/3}$). Therefore, it can be decided that the reaction mechanism in the first stage is the contracting geometrical shape (spherical symmetry). The kinetic equation of this process is $d\alpha/dt=A\exp(-E/RT)3(1-\alpha)^{2/3}$. By substituting $\ln A$, E in the first stage of decomposition obtained through the differential and integral methods into Eq. (7), the values of ΔG in Table 5 were obtained. At the same time, the non-isothermal kinetics data of the TG-DTG curves using the heating rate of 5, 7, 10°C min^{-1} were analyzed again by Achar and MKN methods, and the probable mechanism function obtained was also function No. 13, which is the same as that obtained when the heating rate is 3°C min^{-1}.

Table 4 Kinetic parameters for the first-stage decomposition of $Eu_2(BA)_6(bipy)_2$ obtained by Ozawa method

No.	α	E^a/kJ mol^{-1}	r	No.	α	E^a/kJ mol^{-1}	r
1	0.1	110.6	0.9838	8	0.55	108.60	0.9890
2	0.15	119.27	0.9811	9	0.6	109.00	0.9878
3	0.2	114.55	0.9875	10	0.7	117.20	0.9933
4	0.3	115.57	0.9873	11	0.8	117.37	0.9923
5	0.35	111.20	0.9846	12	0.85	115.20	0.9940
6	0.4	112.50	0.9865	13	0.9	117.70	0.9909
7	0.5	114.30	0.9844				

[a] Average value of E is 114.08 kJ mol^{-1}

Table 5 Calculated values of the kinetics parameters of $Eu_2(BA)_6(bipy)_2$ for stage I

	E/kJ mol^{-1}	ΔG/kJ mol^{-1}	ln(A/s^{-1})	r
Achar method	120.14	120.76	29.86	0.9511
MKN method	123.07	138.67	26.36	0.9811
Average value	121.61	129.72	28.11	0.9661

Conclusions

The thermal decomposition of the $Eu_2(BA)_6(bipy)_2$ occurs in four steps. The reaction mechanism in the first stage is the contracting geometrical shape (spherical symmetry). The kinetic equation of this decomposition reaction is $d\alpha/dt=A\exp(-E/RT)3(1-\alpha)^{2/3}$. The activation energy of the first stage is 121.61 kJ mol^{-1}. The free energy of activation is 129.72 kJ mol^{-1}.

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