ELSEVIER

Thermochimica Acta 306 (1997) 77–80

thermochimica
acta

Studies on the non-isothermal kinetics of thermal decomposition of binuclear europium *m*-methyl benzoate ternary complex with 1,10-phenanthroline

Ping Mu[a,*], Ruifen Wang[b], Liang Zhao[c], Zhijia Zhu[a], Yonghong Guo[a]

[a] *12A-34 Summer Place, Saskatoon Sask, 57H 3w4, Canada*
[b] *Department of Chemistry, Hebei Teachers' University, Shijiazhuang, 050016, P.R. China*
[c] *Department of Computer Science, Hebei Teachers' University, Shijiazhuang 050016, P.R. China*

Received 28 April 1997; accepted 17 June 1997

Abstract

The thermal decomposition of binuclear europium *m*-methyl benzoate ternary complex with 1,10-phenanthroline and its kinetics were studied using non-isothermal condition by thermogravimetric and derivative thermogravimetric (TG–DTG) and infrared (IR) spectroscopic techniques. The non-isothermal kinetic data were analyzed by means of Achar and Coats–Redfern methods. Possible reaction mechanism has been investigated by comparing the kinetic parameter. The kinetic equation for the second stage can be expressed as:

$$d\alpha/dt = A\exp(-E/RT)(1-\alpha)^2$$

The mathematic expression of the kinetic compensation effect is found to be: $\ln A = 0.2175E - 3.4118$. © 1997 Elsevier Science B.V.

Keywords: Europium; Non-isothermal kinetics; Ternary complex; Thermal decomposition

1. Introduction

The rare-earth elements have been widely used as fluorescence and laser material, due to the special physical and chemical properties of the Eu(III) ion. The reports about its synthesis of polybasic complex, structure and spectra are increasing, but the relative studies and the kinetics of thermal decomposition have hardly been read. In this paper, based upon the preparation and the determination of the crystal structure and the luminescence spectra of binuclear europium *m*-methyl benzoate ternary complex with 1,10-phenanthroline [1], we discuss its thermal decomposition procedure by thermogravimetric and derivative thermogravimetric (TG–DTG) and infrared (IR) spectra technique and the corresponding non-isothermal kinetics of the second decomposition by means of Achar [2] and Coats–Redfern [3] methods, respectively.

2. Experimental

2.1. Sample

The ternary complex of binuclear europium *m*-methyl benzoate with 1,10-phenanthroline was prepared as described previously [1].

---

*Corresponding author.

PII S0040-6031(97)00305-5

2.2. Techniques

The IR spectra of the products of thermal decomposition were recorded on Perkin–Elmer 1730 spectrophotometer (KBr wafer, 4000–450 cm^{-1}).

All TG and DTG experiments were carried out on Perkin–Elmer TGA7 thermogravimetric analyzer. The heating rates used were 2.5, 5 and 10°C min^{-1} from ambient to 660°C under nitrogen atmosphere at a flow rate of 40 cm^3 min^{-1}.

The sample weights were 1.3 ± 0.1 mg and everything else was normalized.

3. Results and discussion

3.1. Thermal decomposition process

The TG and DTG curves of [Eu(*m*-MBA)$_3$phen]H_2O (*m*-MBA = $C_8H_7O_2$, *m*-methyl benzoate; phen = $C_{12}H_8N_2$, 1,10-phenanthroline) and the IR spectra of the products of thermal decomposition at various stages are shown in Figs. 1 and 2.

The results of thermal analysis show that the complex was decomposed in three consecutive steps. The first stage started from 25 to 196°C with a mass loss of 2.40 wt%, which corresponds to the loss of a molecule of solvent water (theoretical loss = 2.38 wt%). The TG curve shows degradation in second step started at 196°C and completed at 373°C which was considered to be removal of a phen with a mass loss of 24.43 wt% (theoretical loss = 23.85 wt%).

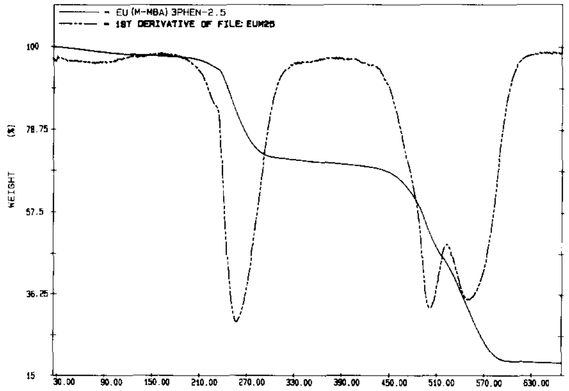

Fig. 1. Thermogravimetric curves (TG and DTG) for [Eu(*m*-MBA)$_3$phen]H_2O.

Fig. 2 shows that the spectra of the residue after decomposition up to 196°C is similar to that of [Eu(*m*-MBA)$_3$phen]H_2O in the region 4000–450 cm^{-1}. The IR absorption band in the region 2400–3500 cm^{-1} indicates the presence of –COOH, in which at 3300 cm^{-1} for the γ_{-OH} band and at 1740 cm^{-1} for the $\gamma_{C=O}$ band, at peaks of 2920, 2850 cm^{-1} for the γ_{-CH_3} bands, 1380, 1460 cm^{-1} for the δ_{-CH_3} bands, in the region 1500–1600 and 750–810 cm^{-1} for the  bands of the *m*-MBA. This shows that the 

molecule is still present in this tested substance, thus, the probable product of thermal decomposition at this stage is Eu(*m*-MBA)$_3$. The third stage in the degradation occurs from 373 to 625°C. Actually, from DTG curve (Fig. 1), this stage includes two steps but there is no clear plateau in the TG curve, namely, the intermediate product is unstable, which continue to lose weight with rising temperature until the formation of Eu_2O_3 with a mass loss of 51.15 wt% (theoretical loss = 50.48 wt%). In fact, the IR spectrum of the product of thermal decomposition up to 625°C is much different from that of the complex [Eu(*m*-MBA)$_3$phen]H_2O. The IR bands of the ligands are almost lost, the rest small peaks are for Eu_2O_3 bands. Therefore, the Eu(III) complex is now completely degraded into Eu_2O_3 with a total loss of 77.98 wt% (theoretical loss = 76.71 wt%).

From the above analysis, the thermal decomposition process of [Eu(*m*-MBA)$_3$phen]H_2O may be expressed as follows:

$$\begin{aligned} &Eu_2(m\text{-MBA})_6(\text{phen})_2(H_2O)_2 \\ &\quad \rightarrow Eu_2(m\text{-MBA})_6(\text{phen})_2 \\ &\quad \rightarrow Eu_2(m\text{-MBA})_6 \rightarrow Eu_2O_3. \end{aligned}$$

3.2. Kinetic studies of the second decomposition stage

Both Achar and Coats–Redfern methods have been used to study the kinetics of the second decomposition stage of the complex.

The integral and differential rate equation are as follows:

$$\ln[(d\alpha/dt)/f(\alpha)] = \ln A - E/RT \qquad (1)$$

$$\ln[g(\alpha)/T^2] = \ln AR/\beta E - E/RT \qquad (2)$$

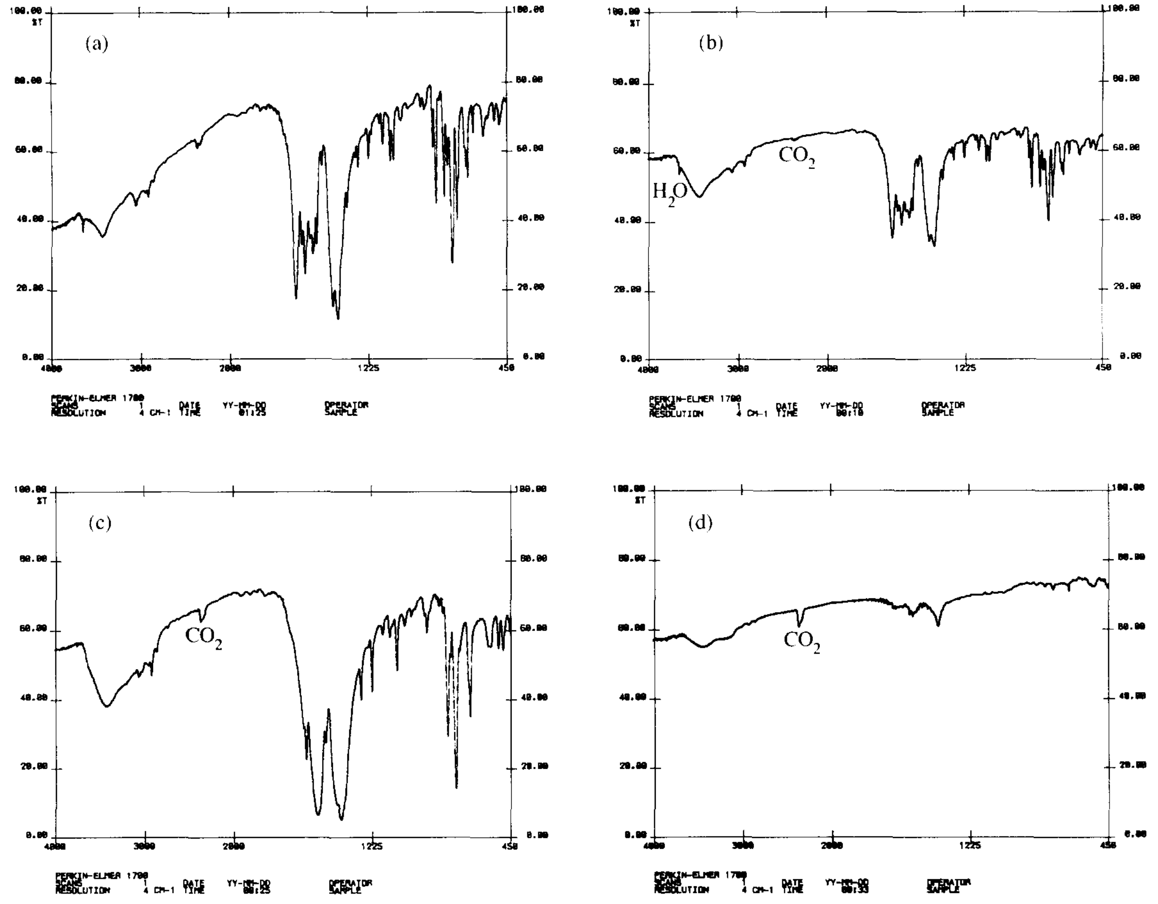

Fig. 2. Infrared spectra of [Eu(m-MBA)$_3$phen]H$_2$O: (a) initial; (b) 196°C; (c) 373°C and (d) 625°C.

where α is the fractional extent of decomposition, T the temperature, A the pre-exponential factor, R the gas constant, E the apparent activation energy, β the linear heating rate, $\mathrm{d}\alpha/\mathrm{d}t$ the rate of conversion, $f(\alpha)$ and $g(\alpha)$ are the differential and integral rate functions, respectively.

The basic parameters of α, T and $\mathrm{d}\alpha/\mathrm{d}T$ obtained from the TG and DTG curves are listed in Table 1. On the basis of 19 kinetic functions in both differential forms commonly used in reviews [4], the kinetic analysis were carried out using a linear least squares method. Calculated kinetic parameters (E, A) and correlation coefficients (r) are also listed in Table 1.

The results show that the values of E and A obtained from the two different methods are approximately the same and the correlation coefficients (r) is better when the function is function No. 18. Therefore, the kinetic equation of the second stage is $\mathrm{d}\alpha/\mathrm{d}t = A\ \exp(-E/Rt)(1-\alpha)^2$. Further, in order to judge the precise values of the most probable mechanism function obtained, in this paper, the Ozawa [5] method is used to calculate the activation energy value of the second thermal decomposition ($E = 169.32$ kJ mol^{-1}, $r = 0.999$). We found that the E and r value are much close to the value given by the differential and integral methods.

According to the frequently used mathematical expression for the kinetic compensation effect $\ln A = aE + b$ [6], where a and b are the compensation parameter, $\ln A$ and E values have also been listed in Table 1. By computing these values, using the linear least-square method with an IBM computer yield the kinetic compensation parameters a and b. The mathematical expression of the kinetic compensation

Table 1
Basic data for [Eu(*m*-MBA)$_3$phen]H$_2$O determined by TG and DTG and kinetic parameter calculated

Function No.	Integral method			Differential method			dα/d*t*	*T*	α
	E (kJ mol^{-1})	ln *A* (s^{-1})	*r*	*E* (kJ mol^{-1})	ln *A* (s^{-1})	*r*			
1	179.51	36.01	0.9367	121.08	25.63	0.8245	0.065	476.07	0.0067
2	193.03	38.69	0.9493	147.52	31.36	0.8923	0.093	483.47	0.0169
3	199.04	38.67	0.9548	159.67	32.79	0.9167	0.133	490.88	0.0330
4	211.57	41.77	0.9648	182.23	38.25	0.9487	0.195	498.31	0.0567
5	167.92	30.88	0.9281	104.51	19.33	0.7835	0.280	505.32	0.0912
6	256.69	52.88	0.9881	249.92	54.63	0.9903	0.459	513.14	0.1455
7	111.77	22.12	0.9757	94.59	21.48	0.9673	0.765	520.55	0.2515
8	71.57	12.92	0.9735	54.39	12.32	0.9503	0.986	527.96	0.3785
9	51.47	8.22	0.9710	34.29	7.66	0.9178	1.022	535.38	0.4994
10	31.36	3.35	0.9648	14.18	2.88	0.7498	0.985	541.31	0.5853
11	21.32	0.77	0.9568	4.13	0.40	0.3321	0.902	548.72	0.6816
12	96.79	17.65	0.9538	60.75	12.60	0.8527	0.802	556.13	0.7651
13	101.36	18.40	0.9615	72.03	14.92	0.9093	0.688	563.55	0.8345
14	85.33	15.43	0.9301	26.90	5.11	0.4715	0.571	570.96	0.8905
15	38.25	4.71	0.9130	−20.18	−5.50	0.5059	0.434	578.37	0.9302
16	22.55	0.88	0.8922	−35.88	−9.22	0.7744	0.262	587.27	0.9548
17	14.70	−1.2	0.8624	−43.73	−11.16	0.8523	0.140	597.65	0.9670
18	153.02	32.39	0.9986	162.28	37.86	0.9961			
19	25.00	2.56	0.8806	128.44	28.97	0.9933			

effect is $\ln A = 0.2175E - 3.4118$, $r = 0.9982$. Thus it can be seen that the differences in the kinetic parameters for a reaction could be determined by both methods of calculation and the kinetic compensation. The kinetic parameters $\ln A$ and E seem to be connected through *a* and *b*. Therefore, we consider that the kinetic compensation parameters may give perfect expression to the thermal decomposition reaction itself.

References

[1] L.P. Jin, R.F. Wang, M.Z. Wang, Chemical Journal of Chinese University 14 (1993) 1195.
[2] B.N. Achar, Proc. Int. Clay, Jerusalem 1 (1996) 67.
[3] A.W. Coats, J.P. Redfern, Nature 201 (1964) 68.
[4] Y.Z. Li, Thermal Analysis, Qinghua University Press, Beijing, 1987, p. 94.
[5] T. Ozawa, Bull. Chem. Soc. Japan 38 (1965) 1881.
[6] J. Zsako, J. Therm. Anal. 9 (1976) 101.