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Synthesis and kinetics of thermal decomposition of complexes of rare earth bromides with glycine

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Abstract

Complexes of rare earth bromides with glycine, $REBr_3 \cdot 3Gly \cdot 3H_2O$ (RE is Ce, Pr, Sm, Eu, Gd, Tb, Dy and Y; Gly is glycine) have been synthesized and characterized by means of chemical analysis, elemental analysis, molar conductivity, thermogravimetry, IR spectra and X-ray diffractometry. The IR spectra of the above complexes indicate that in the complexes glycine is coordinated to rare earth cations through oxygens of the carboxylic group. The thermal decomposition processes of these complexes were studied by means of TG and DTG techniques from ambient to 1000°C.

The kinetics of thermal decomposition of these complexes were studied under non-isothermal conditions by TG techniques. The kinetic parameters (activation energy, E, and pre-exponential factor, A)and the most probable mechanisms of thermal decomposition were obtained from analysis of the TG and DTG curves by using combined integral and differential methods.

Keywords: Bromides; Complexes; Glycine; Kinetics; Rare earth

1. Introduction

Glycine an important amino acid in biology and medicine. Interest in the study of the coodination chemistry of rare earth ions with amino acids is increasing. Thermal investigations of complexes of rare earth chlorides and isothiocyanates with amino acids have been carried out by several groups [1–4], but studies of complexes of rare earth bromides with amino acids are comparatively rare [5,6].

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In this paper, we have prepared and characterized eight complexes, $REBr_3 \cdot 3Gly \cdot 3H_2O$ (RE is Ce, Pr, Sm, Eu, Gd, Tb, Dy and Y Gly is glycine). We have studied the thermal decomposition processes and the kinetics of the thermal decomposition of these complexes under non-isothermal conditions by means of TG and DTG techniques. The most probable mechanism functions and kinetic parameters of the thermal decomposition of these complexes were determined by means of combined differential and integral methods [7,8].

2. Experimental

2.1. Purity of reagents and preparation of the complexes

The purities of the rare earth oxides were better than 99.9%. Glycine was purified by means of recrystallization. The purified glycine was kept in a desiccator containing $CaCl_2$ until its weight became constant.

$REBr_3 \cdot nH_2O$ ($n = 6$ or 7) compounds were prepared as described by Mayer and Zolotov [9].

The complexes $REBr_3 \cdot 3Gly \cdot 3H_2O$ were prepared by the following method. $REBr_3 \cdot nH_2O$ and glycine (in molar ratio 1:3) were dissolved in distilled water, and concentrated at a constant temperature of 50°C. The crystals obtained were filtered off, washed with alcohol and dried over 50% H_2SO_4 to constant weight. The resulting complexes were $REBr_3 \cdot 3Gly \cdot 3H_2O$ (RE is Ce, Pr, Sm, Eu, Gd, Tb, Dy and Y).

2.2. Component analysis of the complexes

The rare earth contents of these complexes were determined by EDTA titration, and the Br^- contents were determined by the Volhard method. The contents of C, H and N were determined with a Perkin-Elmer 240C Elemental Analyzer.

2.3. Physical measurements

The IR spectra of the complexes were recorded with a Nicolet Model FTIR5DX Spectrophotometer. The samples were mounted as mulls in KBr discs and examined between 4000 and 400 cm^{-1}.

The X-ray diffractograms of these complexes were obtained with an X-ray Diffractometer (D/Max-rA, Rigaku, Japan), using copper radiation and a nickel filter.

The molar conductances were determined with a DDS-11A Model Conductometer (made in China) at 25°C.

2.4. TG experimental equipment and conditions

TG experiments were carried out on a Perkin-Elmer TGA 7 Thermogravimetric Analyzer, in an N_2 atmosphere (40 ml min^{-1}) at a heating rate of 10 K min^{-1}. The sample weights were between 3 and 7 mg.

3. Results and discussion

3.1. Component analysis of the complexes

The results of component analysis and the molar conductance values of these complexes are given in Table 1. The formula weights of all complexes agree with the general formula $REBr_3 \cdot 3Gly \cdot 3H_2O$, where RE is Ce, Pr, Sm, Eu, Gd, Tb, Dy and Y.

3.2. Physical measurements

The molar conductance values of aqueous solutions (10^{-3} M) of these complexes were observed in the range 372.8–380.6 $s\,cm^2\,mol^{-1}$, which indicates that these complexes are electrolytes of 1:3 type and that all bromide ions are situated in the outer sphere of the coordination ions.

The IR wavenumbers of some group vibrations in the complexes are listed in Table 2. If we compare the frequencies of some group vibrations of glycine in free and complex forms, the results indicate that glycine retains its zwitterionic structure in its rare earth complexes. This excludes the possibility of coordination of nitrogen to the rare earth ions. There remains the possibility of coordination of the carboxylic group of glycine to the rare earth ions. In free glycine, $\Delta\nu = \nu_{as}(COO^-)\text{-}\nu_s(COO^-) = 226\,cm^{-1}$; in complexes of glycine, because the symmetric stretch frequency of the carboxylic group shifts to higher wavenumbers (violet shift), $\Delta\nu(COO^-) = 197\text{–}219\,cm^{-1}$. This indicates that in the complexes the two oxygens of $-COO^-$ have a higher symmetry and the two oxygens are coordinated to the rare earth ions.

The stretch of $-NH_3^+$ in complexed glycine shifts to a lower wavenumber. In free glycine, $\nu(NH) = 3100\,cm^{-1}$ in complexed glycine, $\nu(NH) = 3038\text{–}3081\,cm^{-1}$. Lower shifts ($19\text{–}62\,cm^{-1}$) in complexed glycine may be due to the formation of hydrogen bonds between glycine and water in the complexes. The O–H stretch of the water molecules in these complexes is observed from 3408 to 3419 cm^{-1}. This shows that these water molecules are hydrogen-bonded.

Table 1
Results of component analysis and molar conductance of the complexes (theoretical values in parentheses)

Complex[a]	RE in %	Br in %	C in %	H in %	N in %	Molar cond./ $s\,cm^2\,mol^{-1}$
$CeBr_3 \cdot 3L \cdot 3H_2O$	21.10(21.26)	35.98(36.37)	10.96(10.93)	3.16(3.21)	6.24(6.38)	379.3
$PrBr_3 \cdot 3L \cdot 3H_2O$	21.35(21.35)	36.21(36.32)	10.87(10.92)	3.16(3.21)	6.20(6.37)	375.4
$SmBr_3 \cdot 3L \cdot 3H_2O$	22.49(22.46)	35.62(35.81)	10.52(10.77)	3.01(3.16)	6.50(6.28)	373.1
$EuBr_3 \cdot 3L \cdot 3H_2O$	22.60(22.65)	35.54(35.73)	10.70(10.74)	3.12(3.15)	6.53(6.26)	372.8
$GdBr_3 \cdot 3L \cdot 3H_2O$	23.39(23.25)	35.42(35.45)	10.79(10.66)	2.96(3.13)	6.41(6.22)	372.9
$TbBr_3 \cdot 3L \cdot 3H_2O$	23.59(23.44)	35.34(35.36)	10.71(10.63)	2.93(3.12)	6.24(6.20)	380.3
$DyBr_3 \cdot 3L \cdot 3H_2O$	24.08(23.85)	35.29(35.18)	10.36(10.57)	2.94(3.10)	6.35(6.17)	375.0
$YBr_3 \cdot 3L \cdot 3H_2O$	14.60(14.63)	38.97(39.43)	12.00(11.86)	3.32(3.48)	7.01(6.91)	380.6

[a] L is Gly.

Table 2
Wavenumbers (cm^{-1}) of some group vibration in the complexes

Approximate description of mode	Vibrations of NH_3^+ group of Gly				Vibration of $-COO^-$ group of Gly			Vibration of $-CH_2$ group of Gly				Vibration of OH group of water
	Asym.		Sym.		Asym.	Sym.		Bend	Stretch	Twist	rock	
	Stretch	Bend	Bend	Rock	Stretch	Stretch	Bend					
Gly	3100 mb[b]	1598 s	1500 s	1128 m 1042 w	1621 s	1395 s	687 m	1437 s	2881 m	1334 s	930 m	–
$CeBr_3 \cdot 3L \cdot 3H_2O^e$	3052 sb	1589 s	1521 s	1102 m	1613 s	1416 s	681 m	1472 s	2905 s	1335 s	915 m	3419 sb
$PrBr_3 \cdot 3L \cdot 3H_2O$	3046 mb	1589 s	1520 s	1102 m	1613 s	1416 s	682 m	1472 s	2905 m	1336 s	915 m	3409 mb
$SmBr_3 \cdot 3L \cdot 3H_2O$	3038 mb	1592 s	1519 s	1103 m	1614 s	1416 s	683 m	1473 s	2905 m	1337 s	916 m	3414 mb
$EuBr_3 \cdot 3L \cdot 3H_2O$	3044 mb	–	1519 s	1103 m	1615 s	1416 s	–	1473	2906 m	1337 s	916 m	3418 mb
$GdBr_3 \cdot 3L \cdot 3H_2O$	3079 mb	1570 s	1500 s	1105 m	1629 s	1417 s	683 m	1467 s	–	1333 s	906 s	3411 mb
$TbBr_3 \cdot 3L \cdot 3H_2O$	3072 mb	1569 s	1500 s	1105 m	1629 s	1415 s	682 m	1468 s	2897 m	1333 s	906 s	3408 mb
$DyBr_3 \cdot 3L \cdot 3H_2O$	3075 mb	1569 s	1499 s	1105 m	1629 s	1415 s	683 m	1467 s	2899 m	1333 s	907 s	3412 mb
$YBr_3 \cdot 3L \cdot 3H_2O$	3081 mb	1570 s	1500 s	1106 m	1632 s	1413 s	682 m	1468 s	2905 m	1334 s	908 s	3416mb

[a] L is glycine.

[b] Intensity of peaks: s, strong; m, medium; w, weak; sb, strong, broad; mb, medium, broad.

Table 3
X-ray diffraction data of $PrBr_3\cdot 3Gly\cdot 3H_2O$, $PrBr_3\cdot 6H_2O$ and glycine

$PrBr_3\cdot 3Gly\cdot 3H_2O$		$PrBr_3\cdot 6H_2O$		Glycine	
2θ/deg	I/I_0	2θ/deg	I/I_0	2θ/deg	I/I_0
7.646	8.5	10.273	54.5	14.944	15.5
11.115	100.0	12.604	32.7	19.109	22.2
14.546	11.6	13.070	15.6	20.239	7.4
15.665	19.3	16.207	18.9	24.037	14.5
16.673	9.4	19.294	26.4	29.307	10.2
18.199	44.9	20.174	74.9	29.996	100.0
22.379	29.0	21.442	100.0	35.512	11.8
23.094	3.3	22.320	15.0	36.679	5.6
24.303	10.1	25.810	14.1	44.537	3.2
26.256	70.1	27.439	27.1		
27.391	6.7	28.209	42.1		
29.054	24.9	31.836	25.4		
29.483	7.9	33.116	18.3		
35.664	13.8	35.513	34.6		
37.528	21.8	40.007	16.8		
41.550	10.6	45.506	10.8		

As an example, the X-ray diffraction data of $PrBr_3\cdot 3Gly\cdot 3H_2O$, $PrBr_3\cdot 6H_2O$ and glycine are listed in Table 3. The X-ray diffraction results indicate that these complexes are very similar in structure. Their maximum values of I/I_0 appear when 2θ equals about 11°, which is different from the X-ray diffraction results of $REBr_3\cdot nH_2O$ and glycine. We can see that the prepared complexes are not simple mixtures of $REBr_3\cdot nH_2O$ and glycine but are new substances.

3.3. Thermal decomposition processes

The TG and DTG curves of the four complexes of Ce, Pr, Sm and Tb are shown in Figs. 1–4. The complexes of Eu and Sm, and the complexes of Gd, Dy, Y and Tb are similar, respectively. The thermal decomposition data of these complexes are listed in Table 4. The TG and DTG curves suggest that the thermal decomposition processes of these complexes are very similar. In the given range of experimental temperatures, they may be described by the following sequences

$$\mathrm{REBr_3\cdot 3Gly\cdot 3H_2O} \xrightarrow[-\mathrm{H_2O}]{\mathrm{I}} \mathrm{REBr_3\cdot 3Gly\cdot 2H_2O} \xrightarrow[-2\mathrm{H_2O}]{\mathrm{II}} \mathrm{REBr_3\cdot 3Gly} \xrightarrow[-2\mathrm{Gly}]{\mathrm{III}}$$

$$\mathrm{REBr_3\cdot Gly} \xrightarrow{\mathrm{IV}} \begin{cases} \mathrm{RE_2O_3}\text{(RE is Sm, Gd, Dy and Y)} \\ \mathrm{REO_2}\text{(RE is Ce)} \\ \mathrm{RE_4O_7}\text{(RE is Tb)} \\ \mathrm{RE_6O_{11}}\text{(RE is Pr)} \end{cases} \tag{1}$$

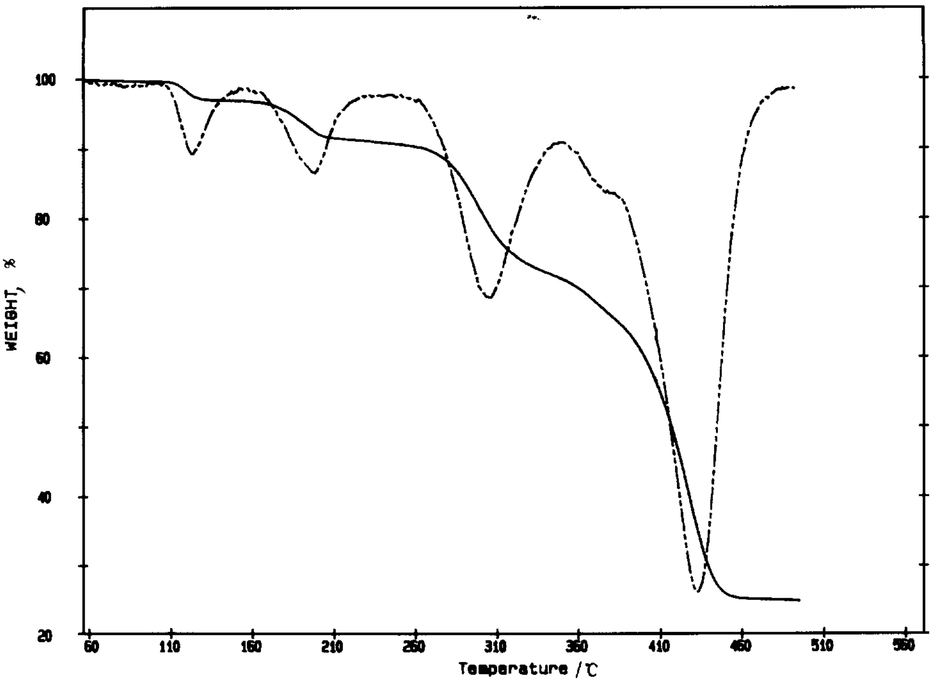

Fig. 1. TG and DTG curves of $CeBr_3 \cdot 3Gly \cdot 3H_2O$ (—, TG – – –, DTG).

$$EuBr_3 \cdot 3Gly \cdot 3H_2O \xrightarrow[-H_2O]{I} EuBr_3 \cdot 3Gly \cdot 2H_2O \xrightarrow[-2H_2O]{II} EuBr_3 \cdot 3Gly \xrightarrow[-3Gly]{III} EuBr_3 \xrightarrow{IV} Eu_2O_3 \tag{2}$$

In the first-stage dehydration, the four complexes $REBr_3 \cdot 3Gly \cdot 3H_2O$ (RE is Gd, Tb, Dy and Y) lose one water molecule in two small steps.

3.4. *Kinetics of thermal decomposition of complexes*

For the kinetic analysis, the differential equation of Achar et al.[10] and the modified Coats–Redfern integral equation [11] were used. The differential and integral equations are

$$\ln\left(\frac{d\alpha/dt}{f(\alpha)}\right) = \ln A - \frac{E}{RT} \tag{3}$$

$$\ln\left(\frac{g(\alpha)}{T^2}\right) = \ln\frac{AR}{\beta E} - \frac{E}{RT} \tag{4}$$

where α is the fraction of material reacted, T is the absolute temperature, β is the linear heating rate, R is the gas constant, E and A are apparent activation energy and

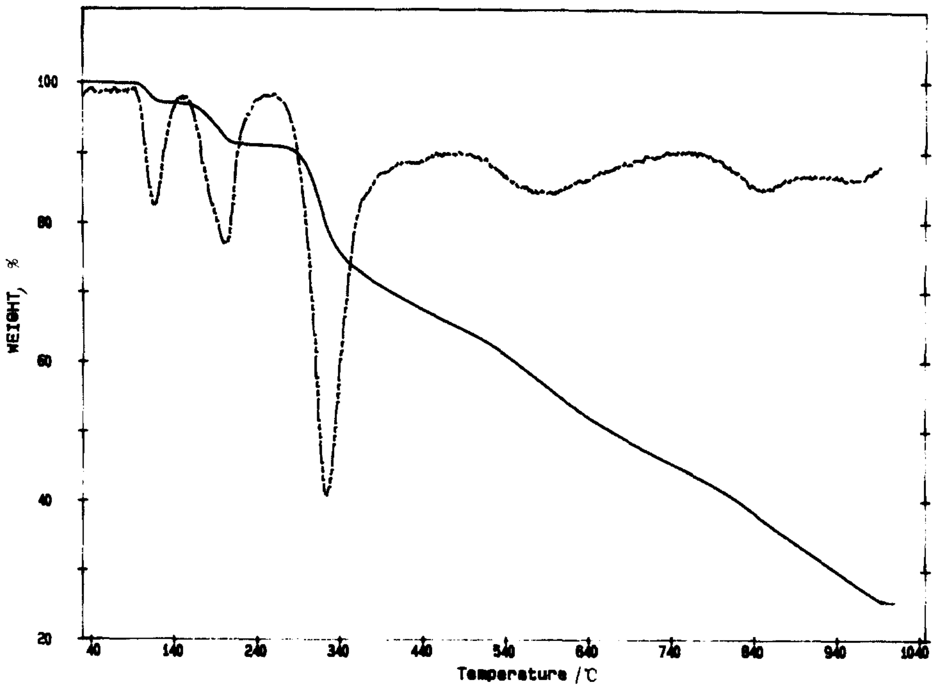

Fig. 2. TG and DTG curves of $PrBr_3 \cdot 3Gly \cdot 3H_2O$ (—, TG; ---, DTG).

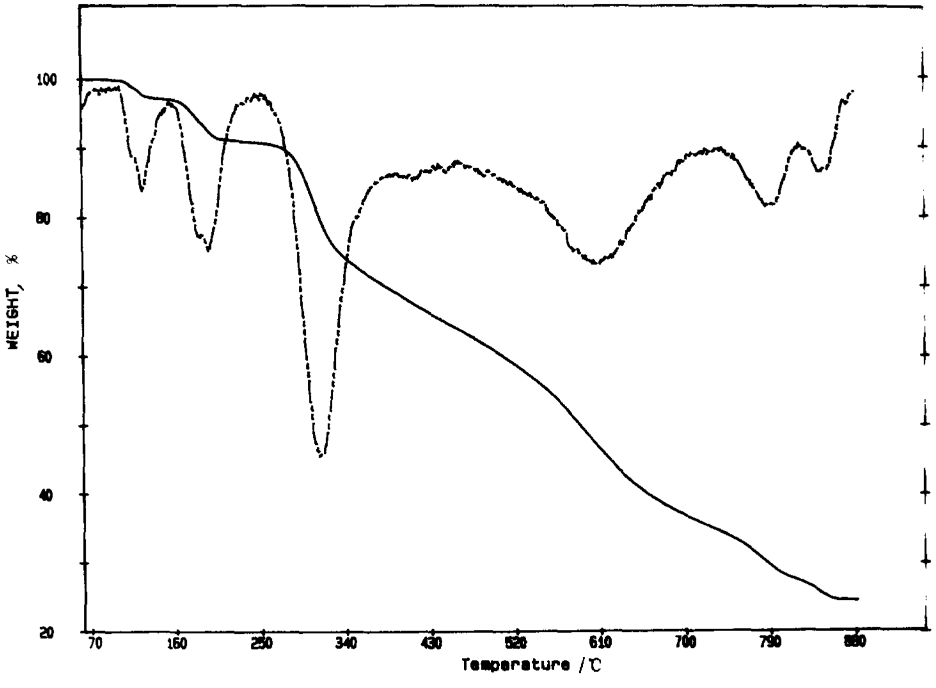

Fig. 3. TG and DTG curves of $SmBr_3 \cdot 3Gly \cdot 3H_2O$ (—, TG; ---, DTG).

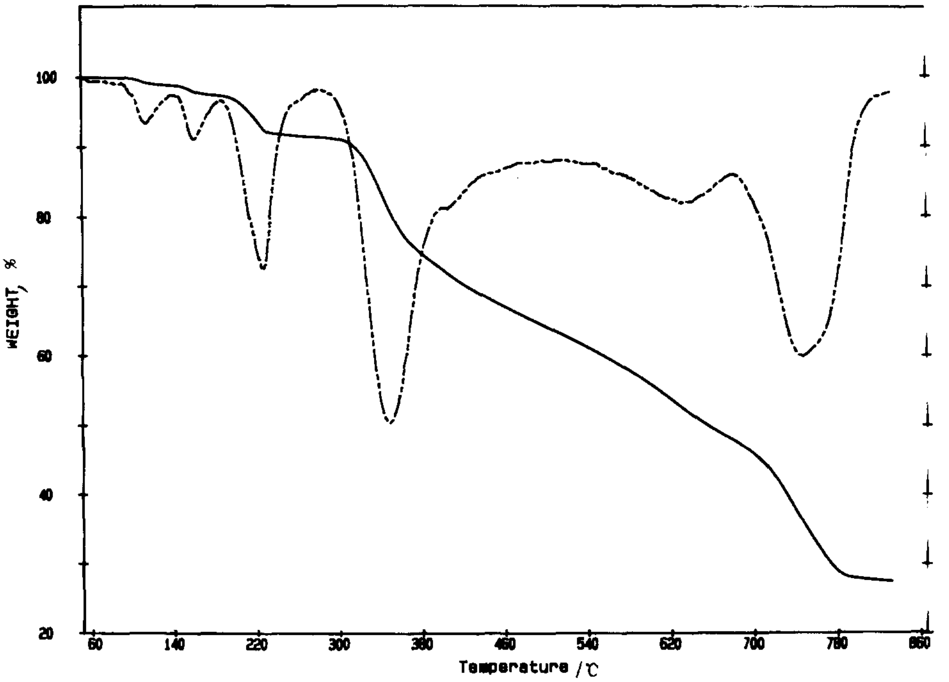

Fig. 4. TG and DTG curves of $TbBr_3 \cdot 3Gly \cdot 3H_2O$ (—, TG; - - -, DTG).

pre-exponential factor, respectively, and $f(\alpha)$ and $g(\alpha)$ are differential and integral mechanism functions, respectively.

We carried out the kinetic analysis for the first three steps of the decomposition of the complexes of Ce, Pr, Sm and Eu, and for the second and third steps for the complexes of Gd, Tb, Dy and Y.

The range of values of α for these steps from the TG and DTG curves are listed in Table 7, below. The original data for these steps from the TG and DTG curves were analyzed by means of Eq(3) and Eq(4) with the possible forms of $f(\alpha)$ and $g(\alpha)$ from Table 5. The kinetic analyses were completed with the linear least-squares method on a computer.

As and example, the data of kinetic analysis in Table 6 clearly show that the the values of E and $\ln A$ from the two methods are approximately same, and that the linear correlation coefficients are better ($r \approx 1$), when the most probable mechanism function is function No. 10 (D3: $f(\alpha) = 1.5(1-\alpha)^{2/3}, [1-(1-\alpha)^{1/3}]^{-1}, g(\alpha) = [1-(1-\alpha)^{1/3}]^2$).

By analogy, we may infer the other thermal decomposition processes for these complexes. The results for the kinetic parameters and the most probable mechanisms for the eight complexes are listed in Table 7.

Although non-isothermal kinetics of thermal analysis as compared with isothermal kinetics when applied to solid state heterogeneous reactions has limitations and failures [12], we have now obtained some reliable results from the non-isothermal

Table 4
Thermal decomposition data of $REBr_3 \cdot 3L \cdot 3H_2O$[a]

Decomp. step of complex	Temp. range/°C	Weight loss in %	
		Calc.	Meas.
$CeBr_3 \cdot 3L \cdot 3H_2O \rightarrow CeBr_3 \cdot 3L \cdot 2H_2O$	104–159	2.73	2.85
$CeBr_3 \cdot 3L \cdot 2H_2O \rightarrow CeBr_3 \cdot 3L$	159–234	5.47	5.75
$CeBr_3 \cdot 3L \rightarrow CeBr_3 \cdot L$	234–355	22.78	20.27
$CeBr_3 \cdot L \rightarrow CeO_2$	355–467	42.91	45.64
$PrBr_3 \cdot 3L \cdot 3H_2O \rightarrow PrBr_3 \cdot 3L \cdot 2H_2O$	89–151	2.73	2.86
$PrBr_3 \cdot 3L \cdot 2H_2O \rightarrow PrBr_3 \cdot 3L$	151–247	5.46	5.95
$PrBr_3 \cdot 3L \rightarrow PrBr_3 \cdot L$	247–422	22.75	22.45
$PrBr_3 \cdot L \rightarrow Pr_6O_{11}$	422–991	43.26	43.20
$SmBr_3 \cdot 3L \cdot 3H_2O \rightarrow SmBr_3 \cdot 3L \cdot 2H_2O$	94–156	2.69	2.88
$SmBr_3 \cdot 3L \cdot 2H_2O \rightarrow SmBr_3 \cdot 3L$	156–244	5.38	6.16
$SmBr_3 \cdot 3L \rightarrow SmBr_3 \cdot L$	244–401	22.43	22.36
$SmBr_3 \cdot L \rightarrow Sm_2O_3$	401–863	43.44	43.84
$EuBr_3 \cdot 3L \cdot 3H_2O \rightarrow EuBr_3 \cdot 3L \cdot 2H_2O$	100–157	2.69	2.61
$EuBr_3 \cdot 3L \cdot 2H_2O \rightarrow EuBr_3 \cdot 3L$	157–235	5.37	5.87
$EuBr_3 \cdot 3L \rightarrow EuBr_3$	235–417	33.57	33.08
$EuBr_3 \rightarrow Eu_2O_3$	417–788	32.14	33.26
$GdBr_3 \cdot 3L \cdot 3H_2O \rightarrow GdBr_3 \cdot 3L \cdot 2H_2O$	70–158	2.66	2.83
$GdBr_3 \cdot 3L \cdot 2H_2O \rightarrow GdBr_3 \cdot 3L$	158–242	5.33	6.30
$GdBr_3 \cdot 3L \rightarrow GdBr_3 \cdot L$	242–408	22.20	22.18
$GdBr_3 \cdot L \rightarrow Gd_2O_3$	408–881	43.01	42.92
$TbBr_3 \cdot 3L \cdot 3H_2O \rightarrow TbBr_3 \cdot 3L \cdot 2H_2O$	89–187	2.66	2.63
$TbBr_3 \cdot 3L \cdot 2H_2O \rightarrow TbBr_3 \cdot 3L$	187–278	5.32	5.90
$TbBr_3 \cdot 3L \rightarrow TbBr_3 \cdot L$	278–445	22.15	23.35
$TbBr_3 \cdot L \rightarrow Tb_4O_7$	445–807	42.29	40.42
$DyBr_3 \cdot 3L \cdot 3H_2O \rightarrow DyBr_3 \cdot 3L \cdot 2H_2O$	68–193	2.64	2.29
$DyBr_3 \cdot 3L \cdot 2H_2O \rightarrow DyBr_3 \cdot 3L$	193–269	5.29	5.87
$DyBr_3 \cdot 3L \rightarrow DyBr_3 \cdot L$	269–433	22.03	22.02
$DyBr_3 \cdot L \rightarrow Dy_2O_3$	433–859	42.67	42.30
$YBr_3 \cdot 3L \cdot 3H_2O \rightarrow YBr_3 \cdot 3L \cdot 2H_2O$	87–179	2.96	2.49
$YBr_3 \cdot 3L \cdot 2H_2O \rightarrow YBr_3 \cdot 3L$	179–276	5.93	5.23
$YBr_3 \cdot 3L \rightarrow YBr_3 \cdot L$	276–414	24.70	24.24
$YBr_3 \cdot 3L \rightarrow Y_2O_3$	414–841	47.84	50.50

[a] RE is Ce, Pr, Sm-Dy and Y; L is Gly.

kinetics of the thermal decomposition for complexes of rare earth bromides with glycine. This is important for both non-isothermal kinetics itself and the properties of rare earth complexes.

4. Conclusions

It can be concluded from the above results (see Eqs. (1) and (2) and Table 4) that the thermal decomposition processes for the complexes of rare earth bromides with glycine

Table 5
The common forms of $f(\alpha)$ and $g(\alpha)$

Funct. no.	Mechanism	$g(\alpha)$	$f(\alpha)$
1	PI	$\alpha^{1/4}$	$4\alpha^{3/4}$
2	A1.5	$[-\ln(1-\alpha)]^{2/3}$	$1.5(1-\alpha)[-\ln(1-\alpha)]^{1/3}$
3	A2	$[-\ln(1-\alpha)]^{1/2}$	$2(1-\alpha)[-\ln(1-\alpha)]^{1/2}$
4	A3	$[-\ln(1-\alpha)]^{1/3}$	$3(1-\alpha)[-\ln(1-\alpha)]^{2/3}$
5	A4	$[-\ln(1-\alpha)]^{1/4}$	$4(1-\alpha)[-\ln(1-\alpha)]^{3/4}$
6	R2	$1-(1-\alpha)^{1/2}$	$2(1-\alpha)^{1/2}$
7	R3	$1-(1-\alpha)^{1/3}$	$3(1-\alpha)^{2/3}$
8	D1	α^2	$1/(2\alpha)$
9	D2	$(1-\alpha)\ln(1-\alpha)+\alpha$	$[-\ln(1-\alpha)]^{-1}$
10	D3	$[1-(1-\alpha)^{1/3}]^2$	$1.5[1-(1-\alpha)^{1/3}]^{-1}(1-\alpha)^{2/3}$
11	D4	$(1-2\alpha/3)-(1-\alpha)^{2/3}$	$1.5[(1-\alpha)^{-1/3}-1]^{-1}$
12	F1	$-\ln(1-\alpha)$	$1-\alpha$
13	F2	$(1-\alpha)^{-1}-1$	$(1-\alpha)^2$
14	F3	$(1-\alpha)^{-2}-1$	$0.5(1-\alpha)^3$

Table 6
Kinetic parameters for the thermal decomposition of $PrBr_3 \cdot 3Gly \cdot 3H_2O$ (step II)

Function No.	Differential method			Integral method		
	E/kJ mol^{-1}	$\ln[A/(s^{-1})]$	r	E/kJ mol^{-1}	$\ln[A/(s^{-1})]$	r
1	−31.27	−11.27	0.8554	15.69	−2.66	0.9323
2	101.65	24.33	0.9940	83.35	16.55	0.9954
3	78.89	18.19	0.9882	60.60	10.38	0.9951
4	56.13	11.94	0.9726	37.84	4.06	0.9943
5	44.75	8.73	0.9539	26.46	0.78	0.9933
6	92.99	21.12	0.9839	104.66	21.24	0.9833
7	111.05	25.59	0.9946	112.10	22.91	0.9885
8	132.27	31.31	0.9125	179.23	40.78	0.9660
9	175.36	42.80	0.9662	201.60	46.28	0.9778
10	230.82	55.75	0.9930	231.87	53.11	0.9893
11	194.71	46.00	0.9799	211.48	47.50	0.9823
12	147.16	36.43	0.9976	128.87	28.68	0.9957
13	255.51	65.68	0.9837	194.12	46.67	0.9952
14	363.86	95.62	0.9727	276.73	69.94	0.9802

take place in four steps and are very similar due to the nature of the rare earth element. These complexes lose water in two steps, then the anhydrous complexes lose two glycine molecules, except $EuBr_3 \cdot 3Gly$ which loses three glycines, and finally form oxides.

The results in Table 7 show that the kinetic mechanisms of the thermal decomposition for $REBr_3 \cdot 3Gly \cdot 3H_2O$ (RE is Ce, Pr, Sm, Eu, Gd, Tb, Dy and Y; Gly is glycine)

Table 7
Kinetic parameters for the thermal decomposition of $REBr_3 \cdot 3Gly \cdot 3H_2O$ (RE is Ce, Pr, Sm, Eu, Gd, Tb, Dy and Y; Gly is glycine)

Complex	Decomp. step	Range of α	E/kJ mol^{-1}			ln [A/(s^{-1})]			Mechanism
			Diff. method	Integral method	Average	Diff. method	Integral method	Average	
$CeBr_3 \cdot 3Gly \cdot 3H_2O$	I	0.0529–0.9355	185.83	187.31	186.57	54.72	52.58	53.65	F1
	II	0.0862–0.9077	282.23	283.74	282.99	68.03	66.36	67.20	D3
	III	0.0755–0.7938	314.18	310.71	312.45	60.72	57.60	59.16	D3
$PrBr_3 \cdot 3Gly \cdot 3H_2O$	I	0.0702–0.9417	175.30	165.92	170.61	53.45	47.71	50.58	F1
	II	0.0793–0.9422	230.82	231.87	231.35	55.75	53.11	54.43	D3
	III	0.0505–0.7155	202.05	195.48	198.77	38.62	34.75	36.69	F2
$SmBr_3 \cdot 3Gly \cdot 3H_2O$	I	0.0960–0.8199	149.53	148.08	148.81	44.16	40.96	42.56	F1
	II	0.0631–0.9054	253.07	260.61	256.84	61.14	61.08	61.11	D3
	III	0.0513–0.7610	171.56	173.74	172.65	32.93	30.83	31.88	F2
$EuBr_3 \cdot 3Gly \cdot 3H_2O$	I	0.0956–0.8647	147.37	145.41	146.39	43.13	39.86	41.50	F1
	II	0.0561–0.8819	273.42	272.17	272.80	66.69	64.13	65.41	D3
	III	0.0546–0.7900	176.28	166.29	171.60	33.89	29.55	31.72	F2
$GdBr_3 \cdot 3Gly \cdot 3H_2O$	II	0.0589–0.8851	367.04	365.45	366.25	91.47	88.72	90.10	D3
	III	0.0559–0.6888	173.09	160.77	166.93	33.27	27.97	30.62	F2
$TbBr_3 \cdot 3Gly \cdot 3H_2O$	II	0.0783–0.9080	321.96	324.28	323.12	74.04	72.56	73.30	D3
	III	0.0530–0.6618	179.31	188.13	183.72	32.31	31.46	31.89	F2
$DyBr_3 \cdot 3Gly \cdot 3H_2O$	II	0.1063–0.9079	336.56	341.91	339.24	78.23	77.02	77.63	D3
	III	0.0561–0.6607	199.34	197.08	198.21	36.46	33.49	34.98	F2
$YBr_3 \cdot 3Gly \cdot 3H_2O$	II	0.0922–0.7828	376.01	385.37	380.69	90.27	90.32	90.30	D3
	III	0.0551–0.7977	222.36	210.31	216.34	41.69	36.42	39.06	F2

depend mainly on the nature of the rare earth elements. Except for the third step of the complex of Ce, the kinetic mechanisms of all the thermal decomposition steps of these complexes have an improved regularity, i.e. the mechanisms are the same in the corresponding steps.

The most probable mechanisms for the thermal decomposition of the four complexes of Ce, Pr, Sm and Eu are F1 ($f(\alpha) = 1 - \alpha$, $g(\alpha) = -\ln(1-\alpha)$) with the loss of one water molecule. The most probable mechanisms for the thermal decomposition of the eight complexes are D3 ($f(\alpha) = 1.5(1-\alpha)^{2/3}[1-(1-\alpha)^{1/3}]^{-1}$, $g(\alpha) = [1-(1-\alpha)^{1/3}]^2$) with the loss of two water molecules, and F2 ($f(\alpha) = (1-\alpha)^2$, $g(\alpha) = (1-\alpha)^{-1} - 1$) with the loss of two or three glycine molecules, except for the Ce complex which is D3 ($f(\alpha) = 1.5(1-\alpha)^{2/3}$ $[1-(1-\alpha)^{1/3}]^{-1}$, ($g(\alpha) = [1-(1-\alpha)^{1/3}]^2$.

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