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KINETICS OF THE COMPLEX OF TERBIUM *o*-METHYLBENZOATE WITH 1,10-PHENANTHROLINE
Synthesis, decomposition mechanism

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Abstract

The complex of [Tb_2(*o*-MBA)$_6$(PHEN)$_2$] (*o*-MBA: *o*-methylbenzoate and PHEN: 1,10-phenanthroline) were synthesized and characterized by elemental analysis and IR spectroscopy. The thermal behavior of [Tb_2(*o*-MBA)$_6$(PHEN)$_2$] in dynamic nitrogen atmosphere was investigated by TG-DTG techniques. The thermal decomposition process of the [Tb_2(*o*-MBA)$_6$(PHEN)$_2$] occurred in three consecutive stages at T_p 294, 427 and 512°C. The kinetic parameters and mechanisms of first decomposition stage from analysis of the TG-DTG curves were obtained by the Malek method.

Keywords: non-isothermal kinetics, *o*-methylbenzoic acid, terbium complex, thermal decomposition, TG-DTG

Introduction

The rare earth complexes with aromatic acid and nitrogen-containing ligands have many special structures and interesting luminous properties, thus arose people's interest to study them. They can be used in many areas such as extraction and separation, germicide, catalyst, luminous materials, functional materials and so on.

In the previous work [1–6], we reported the synthesis, structure, luminescence spectrum and thermal decomposition behavior of some ternary lanthanide complexes with aromatic acid and nitrogen-containing ligands. In this paper, we have prepared the complex of terbium *o*-methylbenzoate with 1,10-phenanthroline. In order to know more about the relationship between its structure and stability, we discussed its thermal decomposition procedure by TG-DTG and IR techniques and the corresponding non-isothermal kinetics by means of the Malek [7–8] method, which pro-

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vides a basis for evaluating the stability and compatibility of the composite luminous materials of the rare earth complexes.

Experimental

Chemicals

All chemicals used were of analytical grade.

Synethesis of complex

3 mmol *o*-HMBA (*o*-methylbenzoic acid) was dissolved in 20 mL 95% C_2H_5OH and its pH was controlled in a range of 6–7 with 1 mol L^{-1} NaOH solution, to which 1 mmol 1,10-phenanthroline dissolved in 10 mL 95% C_2H_5OH was added. The mixed solution was dropped into the $TbCl_3$ solution obtained by 1 mmol $TbCl_3\cdot 6H_2O$ dissolved in 10 mL 95% C_2H_5OH. The mixture was heated under reflux with stirring for 8 h, when a white precipitate formed.

Apparatus and measurements

The carbon, hydrogen and nitrogen analyses were made using a Carlo-Erba model 1106 elemental analyzer. The metal content was assayed using EDTA titration method.

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

TG and DTG experiments for the title compounds were performed using a Perkin Elmer TGA7 thermogravimetric analyzer under a nitrogen atmosphere, at a flow rate of 40 mL min^{-1}. The heating rate used were 3, 5, 7, 10°C min^{-1} from ambient to 925°C and the sample size was 2.1±0.2 mg.

Methodology and kinetic analysis

Kinetics analysis method suggested by Malek et al. [7–8]

Calculation of the activation energy *E*

The calculation of the activation energy is based on multiple-scan methods where several measurements at different heating rates are needed. In the present work, the Kissinger [9] and Ozawa [10] methods were used to obtain *E* values.

Determination of kinetic model

Once the activation energy has been determined, two special functions $Y(\alpha)$ and $Z(\alpha)$ which can easily be obtained by simple transformation of experimental data are defined and a combination of the shape of function $Y(\alpha)$ with parameters α_M and α_p^∞, at which the functions $Y(\alpha)$ and $Z(\alpha)$ have a maximum respectively, allows the determination of the most suitable kinetic model. $Y(\alpha)$ and $Z(\alpha)$ functions can be expressed as follows

$$Y(\alpha)=\left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right)\mathrm{e}^{x} \tag{1}$$

$$Z(\alpha)=\Pi(x)\left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right)\frac{T}{\beta} \tag{2}$$

Calculation of the kinetic exponents *n* (or *m*)

To the calculation of the kinetic exponents, the appropriate equations depending on the kinetic model determined in the above step can be employed.

Calculation of the pre-exponential factor

Knowing the value of the activation energy and kinetic model, the pre-exponential factor can be calculated using equation:

$$A=-\frac{\beta x_{\mathrm{p}}\exp(x_{\mathrm{p}})}{Tf'(\alpha_{\mathrm{p}})} \tag{3}$$

All the computational works were done on an IBM computer using a QBASIC program.

Results and discussion

Elemental analyses and infrared spectra

Analytical results for the complex compared with theoretical calculation results from the proposed formulate are given in Table 1. It can be seen that the experimental data agree with values of theoretical calculation.

Table 1 Elemental analyses of the complex

Complex $[Tb_2(o\text{-MBA})_6(PHEN)_2]$	Elemental content/%			
	C	H	N	Tb
Theoretical values	58.07	3.93	3.76	21.35
Experimental data	58.27	4.20	4.18	21.44

Frequencies of characteristic absorption bands in IR spectra (cm^{-1}) for ligands and complex are listed in Table 2. The IR spectra of the complex show that the absorption valency band of the C=O group, $\nu_{C=O}$ at 1689 cm^{-1} , disappear, whereas the bands of the asymmetric vibrations $\nu_{as(COO^-)}$ at 1606 cm^{-1} and of the symmetric vibrations $\nu_{s(COO^-)}$ at 1418 cm^{-1} are apparent. The values of the splitting for the absorption bands of the valency vibration $\nu_{as(COO^-)}$ and $\nu_{s(COO^-)}\Delta\nu=\nu_{as}-\nu_{s}$ is very high ($\Delta\nu$=188 cm^{-1}). The IR spectra of the complex show that the absorption peak of ν_{O-H} (H_2O) disappear at 3380 cm^{-1}, the absorption band of the $\nu_{C=N}$ at 1644 cm^{-1} are observed to move lower wavenumber. The spectroscopy data suggest that the terbium ion is coordinated with N atoms of 1,10-phenanthroline and O atoms of *o*-methylbenzoate [11, 12]. In the binuclear molecule complex, each Tb^{3+} ions is bound not only to four bridging carboxylate oxygen atoms, but also two bidentate carboxylate oxygen atoms and two nitrogen atoms of phen chelating ligand, giving coordination number of eight [5, 11, 13].

Table 2 Frequencies of characteristic absorption bands in IR spectra (cm^{-1}) for ligands, complex and some intermediate products of the thermal decompositions

Compounds	ν_{O-H}	$\nu_{C=N}$	$\nu_{C=O}$	$\nu_{as(COO^-)}$	$\nu_{s(COO^-)}$	$\Delta\nu=\nu_{as}-\nu_s$
PHEN	3380	1644	–	–	–	–
o-HMBA	–	–	1689	–	–	–
$[Tb_2(o\text{-}MBA)_6(PHEN)_2]$	–	1630	–	1606	1418	188
Intermediate ($Tb_2(o\text{-}MBA)_6$)	–	–	–	1610	1414	186
End product (Tb_4O_7)	–	–	–	–	–	–

Thermogravimetric decomposition data

Thermal analytical data measured at β=5°C min^{-1} for title compound are presented in Table 3. The percentages of mass loss and probable composition of the expelled groups are also given. TG and DTG curves of $[Tb_2(o\text{-}MBA)_6(PHEN)_2]$ using a heating rate of 5°C min^{-1} are shown in Fig. 1.

The thermal decomposition process of $[Tb_2(o\text{-}MBA)_6(PHEN)_2]$ can be divided into three stages. The first stage is at 229–309°C. The TG curve shows that the mass loss corresponding to this temperature range is 24.05% which roughly coincides with

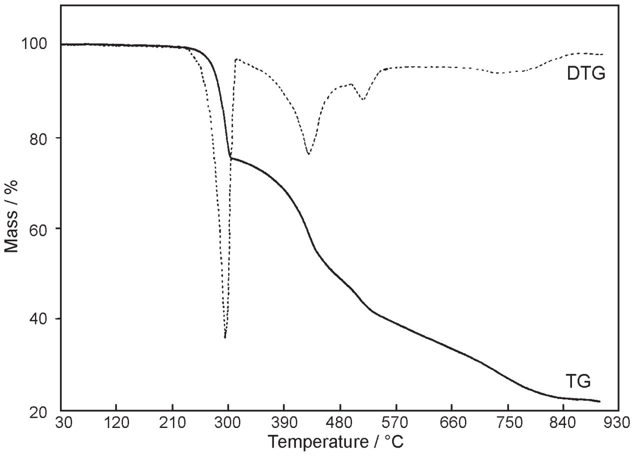

Fig. 1 TG-DTG curves of $[Tb_2(o\text{-}MBA)_6(PHEN)_2]$ using a heating rate of 5°C min^{-1}

the value of 24.20%, calculated for the loss of 2 mol phen from the complex. The IR spectra of the residue at 309°C shows that the absorption band of C=N disappear at 1630 cm^{-1}. The second-stage started from 309–486°C with the mass loss of 27.14%, which corresponds to the loss of 3 mol *o*-MBA and the formation of $\text{Tb}_2(o\text{-MBA})_3$. The theoretical mass loss is 27.23%. The TG curve shows degradation in the third step started at 486 and completed at 848°C which was considered to be removal of a $C_{24}H_{21}O_{2.5}$ with a mass loss of 24.58% (theoretical mass loss is 23.47%). As shown in Table 2, the bands of the asymmetric vibrations $\nu_{\text{as(COO}^-)}$ at 1610 cm^{-1} and of the symmetric vibrations $\nu_{\text{s(COO}^-)}$ at 1414 cm^{-1} for the title complex heated 848°C disappeared.

By 848°C, the complex of terbium *o*-methylbenzoate with 1,10-phenanthroline was completely degraded into Tb_4O_7, with a total loss of 75.77 mass% (theoretical loss is 74.90 mass%). On the bases of experimental and calculated results, the thermal decomposition of $[\text{Tb}_2(o\text{-MBA})_6(\text{PHEN})_2]$ is postulated to proceed as follows:

$$[\text{Tb}_2(o\text{-MBA})_6(\text{PHEN})_2] \rightarrow \text{Tb}_2(o\text{-MBA})_6 \rightarrow \text{Tb}_2(o\text{-MBA})_3 \rightarrow \text{Tb}_4\text{O}_7$$

Table 3 Thermal decomposition data for $[\text{Tb}_2(o\text{-MBA})_6(\text{PHEN})_2]$ in dynamic nitrogen atmosphere from TG and DTG analysis

Stage	Temperature range/°C	DTG peak temp./°C	Mass loss/%		Probable comp. of expelled groups	Intermediate
			TG	Theory		
I	229–309	294	24.05	24.20	$-2C_{12}H_8N_2$	$[\text{Tb}_2(o\text{-BA})_6]$
II	309–486	427	27.14	27.23	–3*o*-MBA	$\text{Tb}_2(o\text{-BA})_3$
III	486–848	512	24.58 75.77[a]	23.47 74.90[a]	$-C_{24}H_{21}O_{2\cdot5}$	Tb_4O_7

[a]Total loss of mass/%

Thermal decomposition kinetics

The activation energy values for the title compound determined by Kissinger and Ozawa methods are listed in Table 4. It can be seen that the values of activation energy obtained by the two methods are in reasonable agreement, and *E* values calculated using the Ozawa method for the title compound are generally independent of the value of α, which has provided a check for the constancy of *E* during the course of reaction, therefore, the average value of *E* obtained using the Ozawa and Kissinger methods was used in the rest of calculations.

The important feature and parameter values thus obtained, such as α_M, α_p^∞ and α_p, corresponding to the maxima of both the $Y(\alpha)$ and $Z(\alpha)$ curves are summarized for the title compound in Table 5. It is evident that the values of these parameters conform to the SB(*m*,*n*) model for title compound. The kinetic parameters calculation for SB model are presented in Table 6.

Table 4 The activation energy values for the first-stage decomposition of [Tb_2(*o*-MBA)$_6$(PHEN)$_2$] obtained by Ozawa and Kissinger methods

No.	α	E_0^a/ kJ mol^{-1}	*r*	No.	α	E_0^a/ kJ mol^{-1}	*r*	Kissinger method	
								E_K /kJ mol^{-1}	*r*
1	0.1	128.28	0.9958	8	0.6	132.3	0.9977	124.24	0.9980
2	0.15	130.81	0.9992	9	0.7	127.37	0.9990	–	–
3	0.2	134.06	0.9995	10	0.8	127.12	0.9982	–	–
4	0.3	131.69	0.9994	11	0.85	128.09	0.9983	–	–
5	0.4	127.35	0.9981	12	0.9	128.99	0.9982	–	–
6	0.5	123.84	0.9989	13	0.95	129.9	0.9980	–	–
7	0.55	133.13	0.9953	–	–	–	–	–	–

[a] The average value of *E* by the Ozawa method at various α values is 129.46 kJ mol^{-1}. The average value of *E* by the Ozawa and Kissinger methods is 126.85 kJ mol^{-1}

Table 5 The characteristic feature of the functions $Y(\alpha)$ and $Z(\alpha)$

β/°C min^{-1}	Shape of $Y(\alpha)$	α_M	α_p^∞	α_p
3	convex	0.3782	0.8388	0.7759
5	convex	0.4041	0.7816	0.7747
7	convex	0.4238	0.8187	0.8214
10	convex	0.3965	0.8265	0.7871

Table 6 Kinetic parameters and mechanism

β/°C min^{-1}	KM[b]	*m*	*n*	ln*A*/s^{-1}	*E*/kJ mol^{-1}
3	SB	0.2771	0.4556	26.16	126.85
5	SB	0.2696	0.3975	25.68	–
7	SB	0.3425	0.4657	25.12	–
10	SB	0.3014	0.4587	24.95	–

[b] KM: kinetic model

Conclusions

The thermal decomposition of the $[Tb_2(o\text{-}MBA)_6(PHEN)_2]$ occurs in three steps. In the first step, the activation energy *E* is 126.85 kJ mol^{-1}, the pre-exponential factor ln*A* is 25.48 and the kinetic model was determined to be SB(*m*, *n*) model.

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