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# KINETICS AND LIFETIME OF THE COMPLEX OF TERBIUM *p*-CHLOROBENZOATE WITH 1,10-PHENANTHROLINE
## Preparation, thermal decomposition

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## Abstract

The complex of [$Tb_2$(*p*-ClBA)$_6$(PHEN)$_2$] [(*p*-ClBA: *p*-chlorobenzoate and PHEN: 1,10-phenanthroline) was prepared and characterized by elemental analysis and IR spectroscopy. The thermal behavior of [$Tb_2$(p-ClBA)$_6$(PHEN)$_2$] in dynamic nitrogen atmosphere was investigated by TG-DTG, SEM and IR techniques. By the kinetic method of processing thermal analysis data put forward by Malek *et al*., it is defined that the kinetic model for the first-step thermal decomposition is SB(m,n). The activation energy $E$ and the pre-exponential factor ln$A$ for this step reaction are 164 kJ mol$^{-1}$ and 32.80, respectively. The lifetime equation at mass loss of 10% was deduced as $\ln\tau=-33.0569+20512.36/T$ by isothermal thermogravimetric analysis.

**Keywords:** kinetics, lifetime, *p*-chlorobenzoic acid, terbium complex, TG-DTG, thermal decomposition

## Introduction

Because of the variation of the bonding forms of carboxylate anions, many different types of crystal structures and interesting fluorescence properties for ternary lanthanide complexes with aromatic acid and nitrogen-containing ligands were obtained [1–7]. Their thermal decomposition behavior have been reported in previous papers [8–15]. In this paper, we have prepared the complex of terbium *p*-chlorobenzoate with 1,10-phenanthroline. And in order to know more about the relationship between its structure and thermal stability, we discussed its thermal decomposition procedure by TG-DTG, SEM and IR techniques and the corresponding non-

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isothermal kinetics by means of the Malek [16, 17] method. The lifetime equation at mass loss of 10% was obtained by isothermal thermogravimetric analysis. This has some directive significance to the determination of the stability of the title compound in different temperatures, and also provides basis for the preparation of the composite luminous materials with good thermal stability.

## Experimental

### *Materials*

All the reagents used were Analar grade and were used without further purification.

### *Preparation of complex [$Tb_2$(p-ClBA)$_6$(PHEN)$_2$]*

A stoichiometric amount of *p*-chlorobenzoic acid was dissolved in 95%$C_2H_5OH$ and its pH was controlled in a range of 6–7 with 1 mol $L^{-1}$ NaOH solution. A quantitative amount 1,10-phenanthroline was also dissolved in 95% $C_2H_5OH$. The two solutions were mixed, and added dropwise into the $TbCl_3$ solution prepared by dissolving $TbCl_3 \cdot 6H_2O$ in 95% $C_2H_5OH$. The mixture was heated under reflux with stirring for a few hours. The white precipitate was formed.

### *Experimental equipment and conditions*

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 Bio-Rad FTS-135 spectrometer, between 4000 and 400 $cm^{-1}$.

A Perkin Elmer TGA7 instrument was used for the isothermal and non-isothermal experiments. The temperatures of isothermal experiment were 260, 275, 290 and 305°C, respectively. Air was used as a static atmosphere. The scanning rate ($\beta$) used in the non-isothermal experiment were 3, 5, 7 and 10°C $min^{-1}$ from ambient to 925°C and the sample size was 2.1±0.2 mg. Nitrogen was used a dynamic atmosphere, at a flow rate of 40 mL $min^{-1}$.

## Methodology and kinetic analysis

### *Kinetic analysis method suggested by Malek et al. [16–17]*

#### Calculation of *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 Ozawa [18] method were used to obtain *E* values.

### Determination of kinetic model

Once the activation energy has been determined, the special functions $Y(\alpha)$ and $Z(\alpha)$ are defined as follows and can be easily obtained by simpled transformation of the experimental data:

$$Y(\alpha)=(\mathrm{d}\alpha/\mathrm{d}t)\,\mathrm{e}^{x} \tag{1}$$

$$Z(\alpha)=\pi(x)(\mathrm{d}\alpha/\mathrm{d}t)T/\beta \tag{2}$$

where $x=E/RT$, and $\pi(x)$ is the approximate function of temperature integral proposed by Sinum–Yang:

$$\pi(x)=(x^3+18x^2+88x+96)/(x^4+20x^3+120x^2+240x+120) \tag{3}$$

By combination of the shape of function $Y(\alpha)$ with parameters $\alpha_\mathrm{m}$, $\alpha_\mathrm{P}$ and $\alpha_\mathrm{p}^\infty$, at which the function $Y(\alpha)$, TG-DTG curve and $Z(\alpha)$ have a maximum, respectively, the most suitable kinetic model function $f(\alpha)$ can be determined. The usually used function $f(\alpha)$ are listed in Table 1 [16, 17].

**Table 1** The kinetic models

| Model | Symbol | $f(\alpha)$ |
|---|---|---|
| Šesták–Berggren equation | SB(m,n) | $\alpha^{m}(1-\alpha)^{n}$ |
| Johnson–Mehl–Avrami | JMA(n) | $n(1-\alpha)[-\ln(1-\alpha)]^{1-1/n}$ |
| Reaction order equation | RO(n) | $(1-\alpha)^{n}$ |
| Two-dimensional diffusion | D2 | $1/[-\ln(1-\alpha)]$ |
| Jander equation | D3 | $3(1-\alpha)^{2/3}/2[1-(1-\alpha)^{2/3}]$ |
| Ginstling–Brounshtein equation | D4 | $3/2[(1-\alpha)^{-1/3}-1]$ |

### Calculation of the kinetic exponents

To 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. The equation is as follows

$$A=-\beta x_\mathrm{p}\exp(x_\mathrm{p})/[T_\mathrm{p}\,f'(\alpha_\mathrm{p})] \tag{4}$$

All the computational work was 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 2. It can be seen that the experimental data agree with values of theoretical calculation.

**Table 2** Elemental analyses of the complex

| Complex [$Tb_2(p\text{-CIBA})_6(PHEN)_2$] | C/% | H/% | N/% | Tb/% |
|---|---|---|---|---|
| Theoretical values | 49.18 | 2.51 | 3.48 | 19.72 |
| Experimental data | 48.60 | 2.73 | 3.14 | 19.45 |

Frequencies of characteristic absorption bands in IR spectra ($cm^{-1}$) for ligands, complex and some intermediate products of the thermal decomposition are given in Table 3. The IR spectra of the complex show that the absorption valency band of the C=O group, $\nu_{C=O}$ at 1684 $cm^{-1}$, disappear, wheras the bands of the asymmetric vibrations $\nu_{as(COO^-)}$ at 1591 $cm^{-1}$ and of the symmetric vibrations $\nu_{s(COO^-)}$ at 1414 $cm^{-1}$ are apparent.

**Table 3** IR absorption for ligands, complex and some intermediate products of the thermal decomposition ($cm^{-1}$)

| Compounds | $\nu_{O-H}$ | $\nu_{C=N}$ | $\nu_{C=O}$ | $\nu_{as(COO^-)}$ | $\nu_{s(COO^-)}$ | $\Delta\nu=\nu_{as}-\nu_s$ |
|---|---|---|---|---|---|---|
| PHEN | 3380 | 1644 | – | – | – | – |
| *p*-CIBA | – | – | 1684 | – | – | – |
| $Tb_2(p\text{-CIBA})_6(PHEN)_2$ | – | 1631 | – | 1591 | 1414 | 177 |
| Intermediate ($Tb_2(p\text{-CIBA})_6$) | – | – | – | 1592 | 1411 | 181 |
| End product ($Tb_4O_7$) | – | – | – | – | – | – |

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 ($\Delta\nu=177 cm^{-1}$). The IR spectra of the complex show that the absorption peak of $\nu_{O-H}$ ($H_2O$) 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 *p*-chlorobenzoate [19–20]. In the binuclear molecule complex, each $Tb^{3+}$ ion is bonded to not only 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 [2, 4, 6].

### *Thermogravimetric decomposition of complex*

TG and DTG curves of [$Tb_2(p\text{-ClBA})_6(PHEN)_2$] at a heating rate of 7°C $min^{-1}$are shown in Fig. 1. The corresponding thermoanalytical data, the peak temperature and temperature range of DTG curve and the percentages of mass loss and probable composition of the expelled groups are given in Table 4. The thermal decomposition process of [$Tb_2(p\text{-ClBA})_6(PHEN)_2$] can be divided into three stages. The first stage is at 269.71–414.56°C. The TG curve shows that the mass loss corresponding to this temperature range is 23.12% which roughly coincides with the value of 22.36%, calculated for the loss of 2 mol PHEN from the complex. The IR spectra of the residue at 415°C shows that the absorption band of C=N disappear at 1631 $cm^{-1}$. The SEM pictures show that the form of the complex changed from a smooth-surface cylinder to a crackled cylinder (Fig. 2). The second-stage starts from 414.56–638.17°C with the mass loss of 37.96%, which corresponds to the loss of 4 mol *p*-ClBA and the formation of [$Tb_2(p\text{-ClBA})_2$].. The theoretical mass loss is 38.61%. The third-stage degradation temperature is in the range of 638.17–850.53°C with the mass loss of 15.40 mass%, in which $Cl_2C_{14}H_8O_{0.5}$ are removed with theoretical loss of 15.83 mass%. As shown in Table 3, the bands of the asymmetric vibrations $\nu_{as_{COO^-}}$ at 1592 $cm^{-1}$ and of the symmetric vibration $\nu_{s_{COO^-}}$ at

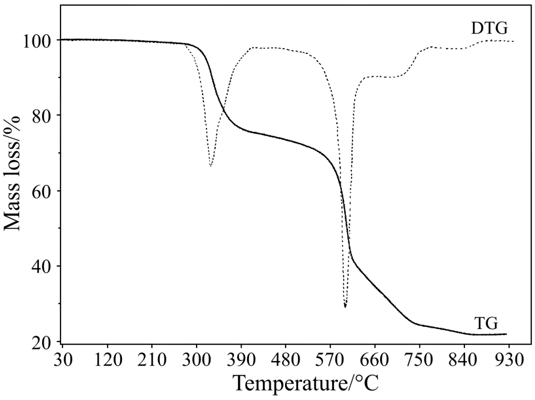

**Fig. 1** TG-DTG curves of [$Tb_2(p\text{-ClBA})_6(PHEN)_2$] at a heating rate of 7°C $min^{-1}$

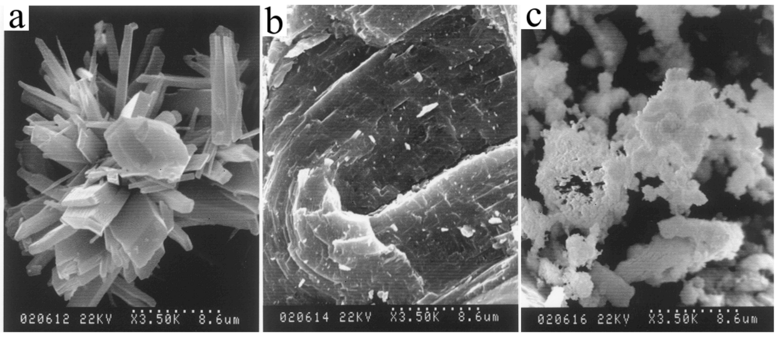

**Fig. 2** Scanning electron micrographs of [$Tb_2(p\text{-ClBA})_6(PHEN)_2$]; a – RT; b – 415 and c – 851°C

**Table 4** Thermal decomposition data for [$Tb_2$(*p*-CIBA)$_6$(PHEN)$_2$] in dynamic nitrogen atmosphere from TG and DTG analysis

| Stage | Temperature range/ °C | DTG peak temperature/ °C | Loss of mass/% | | Probable composition of expelled groups | Intermediate |
|---|---|---|---|---|---|---|
| | | | TG | Theory | | |
| 1 | 269.71–414.56 | 327.36 | 23.12 | 22.36 | $-2C_{12}H_8N_2$ | [$Tb_2$(*p*-CIBA)$_6$] |
| 2 | 414.56–638.17 | 600.19 | 37.96 | 38.61 | –4*p*-CIBA | $Tb_2$(*p*-CIBA)$_2$ |
| 3 | 638.17–850.53 | – | 15.40<br>76.48[a] | 15.83<br>76.76[a] | $-Cl_2C_{14}H_8O_{0.5}$ | $Tb_4O_7$ |

[a] Total loss of mass/%

1411 $\text{cm}^{-1}$ for the title complex heated 851°C disappeared. The SEM pictures for the product obtained at 851°C are also completely different from that of the complex at room temperature. Up to now, the complex of terbium *p*-chlorobenzoate with 1,10-phenanthroline was completely degraded into $Tb_4O_7$, with a total loss of 76.48 mass% (theoretical loss is 76.76 mass%). On the bases of experimental and calculates results, the thermal decomposition of $[Tb_2(p\text{-ClBA})_6(\text{PHEN})_2]$ is postulated to proceed as follows:

$$[Tb_2(p\text{-ClBA})_6(\text{PHEN})_2] \xrightarrow{269.71\text{–}414.56\,^{\circ}\text{C}} [Tb_2(p\text{-ClBA})_6]$$
$$\xrightarrow{414.56-638.17^{\circ}} [Tb_2(p\text{-ClBA})_2] \xrightarrow{638.17\text{–}850.53\,^{\circ}\text{C}} Tb_4O_7$$

*Thermal decomposition kinetics*

Activation energy $E$ is the most important factor for determination of the function $f(\alpha)$[16], so in the condition of not touching the kinetic function, we calculated values of $E$ of the first thermal decomposition step by Ozawa equation [18] using multiple-scan method. The results are listed in Table 5, from which it can be seen that the average values of $E$ is 164 kJ $\text{mol}^{-1}$. The average value was used to calculate function $Y(\alpha)$ and $Z(\alpha)$. The important feature and parameter values thus obtained, such as $\alpha_M$, $\alpha_p^{\infty}$ and $\alpha_p$ corresponding to the maxima of both the $Y(\alpha)$ and $Z(\alpha)$ curves are summarized for the title compound in Table 6. It is evident that the values of these parameters conform to the SB($m$, $n$) model for title compound. The kinetic exponents $m$ and $n$ were calculated from the following equations:

$$\ln[(\mathrm{d}\alpha/\mathrm{d}t)e^{x}]=\ln A+n\ln[\alpha^{p}(1-\alpha)] \quad (5)$$

$$m=pn \quad (6)$$

$$p=\alpha_m/(1-\alpha_m) \quad (7)$$

**Table 5** The activation energy values for the first-stage decomposition of $[Tb_2(p\text{-ClBA})_6(\text{PHEN})_2]$ obtained by Ozawa method

| No. | $\alpha$ | $E_0^a$/kJ $\text{mol}^{-1}$ | $r$ | No. | $\alpha$ | $E_0^a$/kJ $\text{mol}^{-1}$ | $r$ |
|---|---|---|---|---|---|---|---|
| 1 | 0.1 | 174 | 0.9990 | 9 | 0.5 | 178 | 0.9979 |
| 2 | 0.15 | 166 | 0.9978 | 10 | 0.55 | 158 | 0.9959 |
| 3 | 0.2 | 178 | 0.9995 | 11 | 0.6 | 158 | 0.9996 |
| 4 | 0.25 | 182 | 0.9983 | 12 | 0.65 | 143 | 0.9985 |
| 5 | 0.3 | 184 | 0.9986 | 13 | 0.7 | 145 | 0.9964 |
| 6 | 0.35 | 186 | 0.9991 | 14 | 0.75 | 131 | 0.9943 |
| 7 | 0.4 | 185 | 0.9993 | 15 | 0.8 | 122 | 0.9903 |
| 8 | 0.45 | 177 | 0.9981 | 16 | – | – | – |

[a]The average value of $E$ by the Ozawa method at various $\alpha$ values is 164 kJ $\text{mol}^{-1}$

**Table 6** The characteristic feature of the functions $Y(\alpha)$ and $Z(\alpha)$

| $\beta$/°C min$^{-1}$ | Shape of $Y(\alpha)$ | $\alpha_M$ | $\alpha_p^{\infty}$ | $\alpha_p$ |
|---|---|---|---|---|
| 3 | Convex | 0.4439 | 0.4655 | 0.2252 |
| 5 | Convex | 0.4195 | 0.3851 | 0.2170 |
| 7 | Convex | 0.3770 | 0.3888 | 0.2217 |
| 10 | Convex | 0.3576 | 0.3646 | 0.2027 |

The pre-exponential factor $A$ can be calculated using Eq. (4) and the results are listed in Table 7. From it we can see that values of $m$ at various heating rate are 0.1370–0.1604, which is consistent with the values of $0<m<1$ determined in [16].

The thermodynamic parameters of activation can be calculated from the equations [21, 22]:

$$A\exp(-E/RT)=\nu\exp(-\Delta G^{\neq}/RT) \tag{8}$$

$$\Delta H^{\neq}=E-RT \tag{9}$$

$$\Delta G^{\neq =}=\Delta H^{\neq}-T\Delta S^{\neq} \tag{10}$$

The values of entropy, enthalpy and the free energy of activation at the peak temperature obtained on the basis of Eqs (8)–(10) are listed in Table 8.

**Table 7** Kinetic parameters and mechanism

| $\beta$/°C min$^{-1}$ | KM[b] | $m$ | $n$ | ln$A$/s$^{-1}$ | $E$/kJ mol$^{-1}$ |
|---|---|---|---|---|---|
| 3 | SB | 0.1370 | 0.4714 | 33.17 | 164 |
| 5 | SB | 0.1433 | 0.5170 | 32.76 | – |
| 7 | SB | 0.1604 | 0.5630 | 32.76 | – |
| 10 | SB | 0.1414 | 0.5560 | 32.51 | – |

[b] kinetic model

**Table 8** The thermodynamic parameters of title compound

| $\beta$/°C min$^{-1}$ | $E$/ kJ mol$^{-1}$ | ln$A$/s$^{-1}$ | $\Delta H^{\neq}$/ kJ mol$^{-1}$ | $\Delta G^{\neq}$/ kJ mol$^{-1}$ | $\Delta S^{\neq}$/ J mol$^{-1}$ | $T_p$/K |
|---|---|---|---|---|---|---|
| 3 | – | 33.17 | 160 | 150 | 17 | 592.05 |
| 5 | – | 32.76 | 160 | 152 | 13 | 596.29 |
| 7 | – | 32.76 | 160 | 152 | 13 | 600.51 |
| 10 | – | 32.51 | 160 | 153 | 11 | 606.14 |
| Average value | 164 | 32.80 | 160 | 152 | 14 | – |

### *Lifetime*

Dakin [13] has proposed and proved that the general lifetime formula of materials is

$$\ln\tau = a/T + b \qquad (11)$$

where $\tau$ is the lifetime at temperature $T$(K), $a$ and $b$ are constant. In this paper, the mass loss lifetime was measured by isothermal temperature TG at 260, 275, 290 and 305°C and listed in Table 9. By substituting the value in Table 9 into Eq. (11), the constant $a$, $b$ and linear correlation coefficients $r$ were obtained by the linear least squares method. The lifetime equation is: $\ln\tau = -33.0569 + 20512.36/T$. Linear correlation coefficients $r$ is 0.9989.

**Table 9** The lifetime of the $[Tb_2(p\text{-}ClBA)_6(PHEN)_2]$ by isothermal temperature TG

| $T$/°C | $T_{10\%}$/min | $T$/°C | $T_{10\%}$/min |
|---|---|---|---|
| 260 | 235.49 | 290 | 27.23 |
| 275 | 75.65 | 305 | 11.93 |

## Conclusions

The thermal decomposition mechanism of $[Tb_2(p\text{-}ClBA)_6(PHEN)_2]$ could be expressed by the scheme shown in the text. The kinetic model obtained by employing Malek method for the first stage decomposition of the title compound was SB($m,n$). The activation energy $E$ and the pre-exponential factor $\ln A$ for this step reaction are 164 kJ $mol^{-1}$ and 32.80, respectively. The lifetime equation at mass loss of 10% was deduced as $\ln\tau = -33.0569 + 20512.36/T$ by isothermal thermogravimetric analysis.

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