Journal of Thermal Analysis and Calorimetry, Vol. 87 (2007) 3, 841–845

STUDY OF ISOTHERMAL DECOMPOSITION OF LANTHANIDE MIXED COMPLEXES WITH 2,2,6,6-TETRAMETHYL-3,5-HEPTANODIONE AND 1,10-PHENANTHROLINE

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Isothermal decomposition kinetic of three lanthanide mixed complexes with the general formula of Ln(thd)3phen (where *Ln*=Nd^{3+}, Sm^{3+} or Er^{3+}, *thd*=2,2,6,6-tetramethyl-3,5-heptanodione and *phen*=1,10-phenanthroline) has been studied in this work. The powders were characterized by their melting point, elemental analysis, FTIR spectroscopy and thermogravimetry. The isothermal TG curves have been recorded under the same conditions at 265–285, 265–285 and 250–270°C for Nd$(thd)_3$phen, Sm$(thd)_3$phen and Er$(thd)_3$phen, respectively.

The kinetic parameters, i.e. activation energy, reaction order and frequency factor were obtained through the technique of lineal regression using the relation $g(\alpha)=kt+k_0$. The analysis was done at decomposed fractions between 0.10–0.90. The values of activation energy were: 114.10, 114.24 and 115.04 kJ mol^{-1} for the Nd$(thd)_3$phen, Sm$(thd)_3$phen and Er$(thd)_3$phen complexes, respectively. The kinetic models that best described the isothermal decomposition reaction the complexes were R1 and R2. The values of activation energy suggests the following decreasing order of stability: Nd$(thd)_3$phen<Sm$(thd)_3$phen<Er$(thd)_3$phen.

Keywords: *activation energy, β-diketone, isothermal kinetic, lanthanide, mixed complexes*

Introduction

β-diketonate complexes of a number of metals are routinely employed as convenient precursors for the metal-organic chemical vapour deposition (MOCVD). Metal-organic chemical vapor deposition has been studied extensively as a method for preparing thin films of various metals, including copper as well [1–3].

Actually, numerous researchers are interested in the coordination of compounds with organic ligands and metals, as lanthanide ion complexes with β-diketone, which can act as excellent conversion molecular devices (LCMD) [4–10]. Among other properties, the synthesis, luminescence, quantum yields, spectroscopic characteristics, structure of these complexes, including the possibility of thin film production using these materials have been discussed, but little is known about their thermal decomposition kinetics [11–15].

Thus, this work aims to determine kinetic parameters of isothermal decomposition of three Ln$(thd)_3$phen type lanthanide mixed complexes, where *thd* represents the β-diketone 2,2,6,6-tetramethyl-3,5-heptanodione, *phen* is 1,10-phenanthroline and *Ln* are the lanthanide ions, Nd^{3+}, Sm^{3+} or Er^{3+}.

Experimental

Sample

The starting materials to synthesize the complex were high purity of Nd_2O_3, Sm_2O_3 and Er_2O_3 (99%); 2,2,6,6-tetramethyl-3,5-heptanodione and 1,10-phenanthroline supplied by Aldrich Chemical Co. The complexes were synthesized by reacting the metal salt of chloride with β-diketone and the other ligands [10].

Instrumental methods

The melting temperatures of two compounds were determined by means of a Microquímica model MQAPF-301 apparatus. Microanalysis for carbon, hydrogen and nitrogen were performed with a Thermoquest CE Instruments model EA 1110 CHNS-O. The metal content of the complexes was determined by complexometric titration using bromopyrogallol red as indicator and EDTA solution [16].

Infrared spectra were recorded in KBr pellets in the range of 4000–400 cm^{-1} using BOMEM, model MB-102 series FTIR Spectrophotometer. The UV-Vis absorption spectra were recorded by a PerkinElmer UV-Vis Spectrophotometer Lambda 6 Model 2688-002.

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1388–6150/$20.00

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Thermoanalytical measurements

The DSC curves were recorded using Shimadzu DSC-50 differential scanning calorimeter in 25–400°C temperature range of using aluminum crucible at a heating rate of 10°C min^{-1} under flowing nitrogen (50 mL min^{-1}).

Thermogravimetric curves were obtained using a Shimadzu TGA-50 thermobalance using an alumina crucible at a heating rate of 5, 10 and 15°C min^{-1} between 25–400°C under flowing nitrogen (50 mL min^{-1}). The initial sample masses were about 3.0 mg.

The isothermal TG curves were performed under the same conditions in 265–285, 265–285 and 250–270°C temperature intervals for $Nd(thd)_3phen$, $Sm(thd)_3phen$ and $Er(thd)_3phen$, respectively. The TG and DSC curves were analyzed by the aid of the TASYS software supplied by Shimadzu.

Kinetic parameters

The application of the isothermal method in the study of the thermal decomposition reactions of the complexes aims to propose the possible mechanisms for which the reaction is processed, as well as to determine the kinetic parameters, activation energy (*E*) and frequency factor (*A*).

The selection of the mechanisms was accomplished applying different models for the heterogeneous reactions in the solid-state [17–20]. The experimental data were treated by lineal regression using: $g(\alpha)=kt+k_0$. The kinetics parameters were estimated for values of decomposed fraction between 0.10 and 0.90.

Results and discussion

The studied complexes were synthesized from the lanthanide chloride salts using 2,2,6,6-tetramethyl-3,5-heptanodione (*thd*) and 1,10-phenanthroline (*phen*) ligands resulting solid powder complexes which are soluble in organic solvents, as alcohols, chloroform and acetone, and insoluble in water. The IR vibrational spectra provided good evidence that the metal ion is coordinated to the ligands through the C=O and C–N groups [15]. The most important IR bands and the main characteristics of the studied complexes in this work are shown in Table 1.

According to the TG/DSC data, for $Nd(thd)_3phen$ and $Sm(thd)_3phen$ the thermal decomposition started after their melting while for $Er(thd)_3phen$ the thermal decomposition started in solid phase as it is shown in Table 1.

All complexes showed one-step thermal decomposition. The reaction for the $Nd(thd)_3phen$ complex took place between 213–347°C resulting 96.7% of mass loss. $Sm(thd)_3phen$ exhibited 97.8% mass loss in the 222–343°C temperature interval. On the other hand, the $Er(thd)_3phen$ complex decomposed between 214–330°C where the measured mass loss was 93.6%.

The selection of temperatures for the isothermal experiments based on the dynamic TG curves recorded at 10°C min^{-1} heating rate. Figures 1–3 show thermal decomposition profiles under isothermal conditions.

A3, A4, R1 and R2 models described the best of the decomposition processes. The obtained rate constants (*k*), linear correlation coefficient (*r*) and standard deviation (*s*) are summarized in Table 2.

The kinetic parameters, activation energy (E_a) and frequency factor (*A*) were determined graphically using the Arrhenius equation. These values are listed in Table 3.

The selection of the best representative model for the isothermal decomposition reaction was done according to the highest linear correlation coefficient and the lowest standard deviation value. The most representative kinetic models for the thermal decomposition of the complexes under isothermal conditions were R1 for $Sm(thd)_3phen$, R2 for $Nd(thd)_3phen$ and $Er(thd)_3phen$. Figures 4–6 show the curves of decomposed fraction *vs.* time for those models that describe well the isothermal decomposition of the complexes.

R1 model indicates that the mechanism is controlled by one-dimensional phase-boundary (zero order) and is defined by the $g(\alpha)=1-(1-\alpha)$ function. R2 model indicates that the mechanism is controlled by phase-boundary reaction (cylindrical symmetry) and is defined by the $g(\alpha)=[1-(1-\alpha)^{1/2}]$ function indicating a mean reaction order.

According to the apparent activation energy values obtained for the isothermal decomposition of the complexes, the following stability order can be established: $Nd(thd)_3phen<Sm(thd)_3phen<Er(thd)_3phen$.

Table 1 Characteristics of the studied complexes

Complex	Molecular formula	Molar mass/g mol^{-1}	IR/cm^{-1}		UV-Vis/nm	Melting temperature	
			$\nu_{C=O}$	ν_{C-N}		*T*/°C	obs*
$Nd(thd)_3phen$	$Nd(C_{45}H_{65}O_6N_2)$	874.3	1574	1226	230; 266	222.5	D/M
$Sm(thd)_3phen$	$Sm(C_{45}H_{65}O_6N_2)$	880.4	1574	1227	228; 268	232.0	D/M
$Er(thd)_3phen$	$Er(C_{45}H_{65}O_6N_2)$	897.3	1578	1227	231; 269	224.7	D

*D/M→decomposition/melting; D→decomposition.

Table 2 Rate constant (k), linear correlation coefficient (r), standard deviation (s) obtained by equation $g(\alpha)=kt+k_0$

Model	Parameters	Isothermal temperature/°C				
Nd(thd)$_3$phen		265	270	275	280	285
A3	k/s^{-1}	$3.8\cdot10^{-4}$	$4.8\cdot10^{-4}$	$5.9\cdot10^{-4}$	$7.7\cdot10^{-4}$	$9.6\cdot10^{-4}$
	r	0.998	0.998	0.999	0.999	0.998
	s	0.0108	0.0106	0.0104	0.0104	0.0109
A4	k/s^{-1}	$2.9\cdot10^{-4}$	$3.7\cdot10^{-4}$	$4.6\cdot10^{-4}$	$6.0\cdot10^{-4}$	$7.4\cdot10^{-4}$
	r	0.998	0.998	0.998	0.998	0.998
	s	0.0102	$9.60\cdot10^{-3}$	$9.50\cdot10^{-3}$	$9.06\cdot10^{-3}$	$9.53\cdot10^{-3}$
R1	k/s^{-1}	$4.0\cdot10^{-4}$	$5.0\cdot10^{-4}$	$6.1\cdot10^{-4}$	$8.1\cdot10^{-4}$	$1.0\cdot10^{-3}$
	r	0.999	0.999	0.999	0.999	0.999
	s	$3.8\cdot10^{-3}$	$3.4\cdot10^{-3}$	$3.6\cdot10^{-3}$	$3.5\cdot10^{-3}$	$3.1\cdot10^{-3}$
R2	k/s^{-1}	$3.0\cdot10^{-4}$	$3.8\cdot10^{-4}$	$4.6\cdot10^{-4}$	$6.1\cdot10^{-4}$	$7.5\cdot10^{-4}$
	r	0.993	0.993	0.993	0.992	0.992
	s	0.0197	0.0207	0.0207	0.0214	0.0218
Sm(thd)$_3$phen		265	270	275	280	285
A3	k/s^{-1}	$4.2\cdot10^{-4}$	$5.6\cdot10^{-4}$	$6.8\cdot10^{-4}$	$8.3\cdot10^{-4}$	$1.1\cdot10^{-3}$
	r	0.998	0.998	0.998	0.998	0.998
	s	0.0123	0.0116	0.0124	0.0126	0.0130
A4	k/s^{-1}	$3.3\cdot10^{-4}$	$4.4\cdot10^{-4}$	$5.3\cdot10^{-4}$	$6.5\cdot10^{-4}$	$8.4\cdot10^{-4}$
	r	0.998	0.998	0.998	0.998	0.998
	s	0.0101	$9.2\cdot10^{-3}$	$9.5\cdot10^{-3}$	$9.3\cdot10^{-3}$	$9.2\cdot10^{-3}$
R1	k/s^{-1}	$4.4\cdot10^{-4}$	$5.8\cdot10^{-4}$	$7.1\cdot10^{-4}$	$8.7\cdot10^{-4}$	$1.1\cdot10^{-3}$
	r	0.999	0.999	0.999	0.999	0.999
	s	$1.7\cdot10^{-3}$	$2.7\cdot10^{-3}$	$2.9\cdot10^{-3}$	$3.7\cdot10^{-3}$	$4.8\cdot10^{-3}$
R2	k/s^{-1}	$3.3\cdot10^{-4}$	$4.4\cdot10^{-4}$	$5.3\cdot10^{-4}$	$6.5\cdot10^{-4}$	$8.4\cdot10^{-4}$
	r	0.992	0.992	0.991	0.991	0.990
	s	0.0224	0.0226	0.0233	0.0240	0.0249
Er(thd)$_3$phen		250	255	260	265	270
A3	k/s^{-1}	$3.7\cdot10^{-4}$	$5.1\cdot10^{-4}$	$7.0\cdot10^{-4}$	$8.3\cdot10^{-4}$	$9.8\cdot10^{-4}$
	r	0.998	0.999	0.999	0.999	0.999
	s	0.0112	$9.7\cdot10^{-3}$	0.0103	$8.3\cdot10^{-3}$	$8.9\cdot10^{-3}$
A4	k/s^{-1}	$2.9\cdot10^{-4}$	$3.9\cdot10^{-4}$	$5.5\cdot10^{-4}$	$6.4\cdot10^{-4}$	$7.6\cdot10^{-4}$
	r	0.997	0.997	0.998	0.998	0.998
	s	0.0133	0.0117	$9.27\cdot10^{-3}$	0.0101	0.0115
R1	k/s^{-1}	$3.8\cdot10^{-4}$	$5.2\cdot10^{-4}$	$7.3\cdot10^{-4}$	$8.6\cdot10^{-4}$	$1.0\cdot10^{-3}$
	r	0.998	0.999	0.999	0.999	0.998
	s	0.0131	0.0100	$3.81\cdot10^{-3}$	$9.37\cdot10^{-3}$	0.0123
R2	k/s^{-1}	$3.0\cdot10^{-4}$	$4.0\cdot10^{-4}$	$5.5\cdot10^{-4}$	$6.6\cdot10^{-4}$	$7.8\cdot10^{-4}$
	r	0.997	0.996	0.993	0.995	0.996
	s	0.0132	0.0156	0.0210	0.0174	0.0147

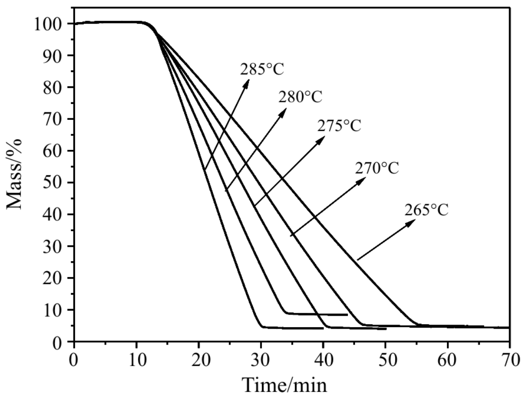

Fig. 1 Isothermal curves of Nd(thd)$_3$phen complex

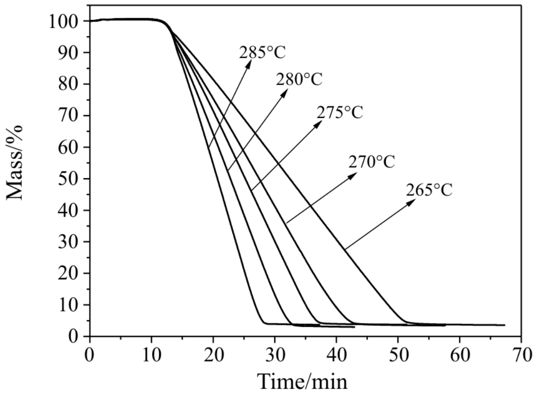

Fig. 2 Isothermal curves Sm(thd)$_3$phen complex

Table 3 Kinetic parameters determined by isothermal thermogravimetry, according to Arrhenius law

Complex	Parameter	Mechanism			
		A3	A4	R1	R2
Nd(thd)$_3$phen	E_a/kJ mol^{-1}	114.7	114.9	114.6	114.1
	A/s^{-1}	$5.3\cdot10^{7}$	$4.3\cdot10^{7}$	$5.4\cdot10^{7}$	$3.6\cdot10^{7}$
	r	0.998	0.998	0.998	0.998
	s	0.0199	0.0200	0.0200	0.0197
Sm(thd)$_3$phen	E_a/kJ mol^{-1}	114.3	114.5	114.3	113.7
	A/s^{-1}	$5.4\cdot10^{7}$	$4.4\cdot10^{7}$	$5.5\cdot10^{7}$	$3.6\cdot10^{7}$
	r	0.997	0.997	0.997	0.997
	s	0.0279	0.0277	0.0276	0.0286
Er(thd)$_3$phen	E_a/kJ mol^{-1}	115.3	115.4	115.1	115.0
	A/s^{-1}	$1.3\cdot10^{8}$	$1.0\cdot10^{8}$	$1.3\cdot10^{8}$	$9.6\cdot10^{7}$
	r	0.988	0.987	0.987	0.989
	s	0.0687	0.0703	0.0703	0.0636

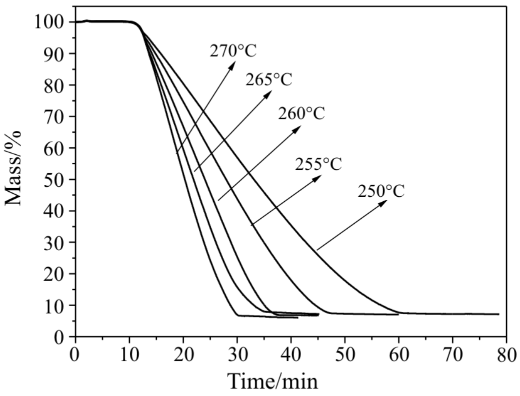

Fig. 3 Isothermal curves of Er(thd)$_3$phen complex

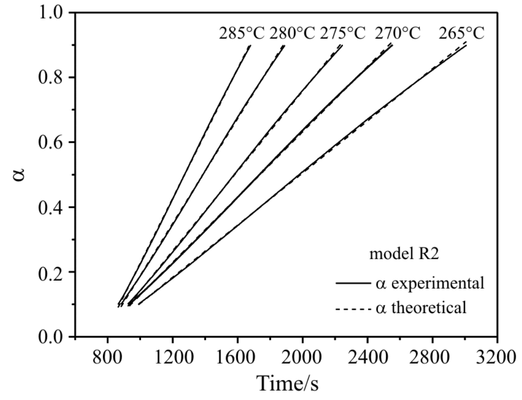

Fig. 4 Isothermal decomposition of Nd(thd)$_3$phen complex according to R2 model

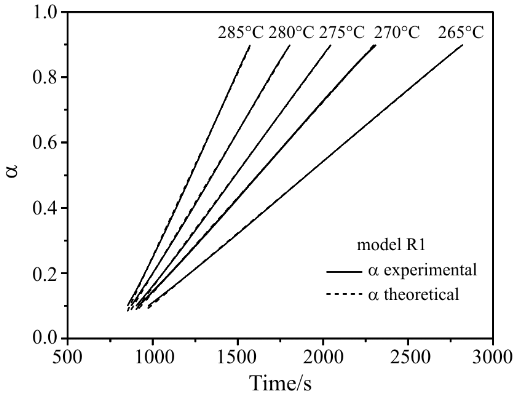

Fig. 5 Isothermal decomposition of Sm(thd)$_3$phen complex according to R1 model

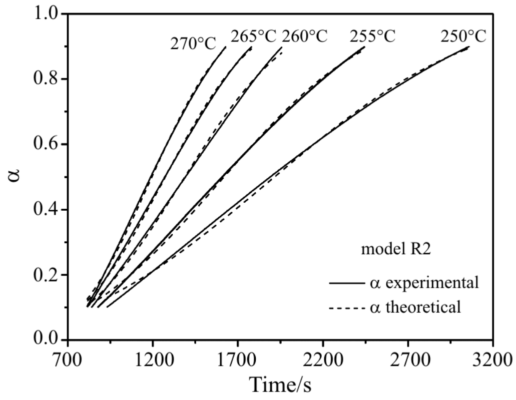

Fig. 6 Isothermal decomposition of Er(thd)$_3$phen complex according to R2 model

Conclusions

The best describing kinetic models (A2, A3, R1 and R2) are in agreement with the results of isothermal decomposition experiments. The best model for the decomposition of Sm(thd)$_3$phen is R1 while for Nd(thd)$_3$phen and Er(thd)$_3$phen is R2.

According the TG/DSC data it was verified that the mass loss started in solid-state. On the base of the isothermal kinetic analysis, according to the activation energies the following stability order was observed: Nd(thd)$_3$phen<Sm(thd)$_3$phen<Er(thd)$_3$phen.

References

1 T. J. Marks, Pure Appl. Chem., 67 (1995) 313.
2 P. Doppelt, Coord. Chem. Rev., 178–180 (1998) 1785.
3 M. J. DelaRosa, K. K. Banger, S. Higashiya, S. C. Ngo, D. H. Hunt, K. S. Bousman, P. J. Toscano and J. T. Welch, J. Fluorine Chem., 123 (2003) 109.
4 J. M. Lehn, Angew. Chem. Int. Ed. Engl., 29 (1990) 1304.
5 N. Sabbatini, M. Guardigli and J. M. Lehn, Coord. Chem. Rev., 123 (1993) 201.
6 N. Sebbtini, M. Guardigli, I. Manet, R. Ungaro, A. Casnati, R. Ziessel, G. Ulrich and J. M. Lehn, Pure Appl. Chem., 67 (1995) 137.
7 Z. Rzaczynska, A. Ostasz, M. Sikorska-Iwan, H. Gluchowska, E. Olszewska and S. Pikus, J. Therm. Anal. Cal., 84 (2006) 575.
8 A. G. Souza, M. L. A. Tavares, D. M. A. Melo, M. M. Conceição, J. G. P. Espinola and C. Airoldi, J. Therm. Anal. Cal., 67 (2002) 351.
9 T. S. Martins, J. R. Matos, G. Vicentini and P. C. Isolani, J. Therm. Anal. Cal., 86 (2006) 351.
10 C. R. S. Morais, A. G. Souza and P. A. Santa-Cruz, J. Alloys Compd., 344 (2002) 415.
11 C. S. M. Morais, W. S. Lopes, A. G. Souza and P. A. Santa-Cruz, J. Metastable Nanocryst. Mater., 20–21 (2004) 462.
12 W. S. Lopes, C. R. S. Morais and A. G. Souza, Mater. Sci. Forum, 530–531 (2006) 506.
13 R. Q. Albuquerque, G. B. Rocha, O. L. Malta and P. Porcher, Chem. Phys. Lett., 331 (2000) 519.
14 H. J. Batista, A. V. M. de Andrade, R. L. Longo, A. M. Simas, G. F. de Sá and L. C. Thompson, Inorg. Chem., 37 (1998) 3542.
15 W. S. Lopes, C. R. S. Morais, A. G. Souza and V. D. Leite, J. Therm. Anal. Cal., 79 (2005) 343.
16 J. Körbl and R. Piribil, Xilenol orange: new indicator for EDTA titration, Ed. Chemist Analyst, New Jersey 1990.
17 M. I. Yoshida, M. M. Braga and J. C. Machado, Thermochim. Acta, 237 (1994) 347.
18 L. S. Barreto, C. D. Pinheiro and A. G. Souza, Thermochim. Acta, 328 (1999) 231.
19 M. C. N. Machado, C. D. Pinheiro, L. M. Nunes, J. C. Machado and A. G. Souza, Thermochim. Acta, 328 (1999) 201.
20 J. H. G. Rangel, S. F. Oliveira, J. G. P. Espínola and A. G. Souza, Thermochim. Acta, 328 (1999) 187.

DOI: 10.1007/s10973-006-7785-x