Journal of Thermal Analysis and Calorimetry, Vol. 75 (2004) 591–597

KINETIC STUDY OF DIPIVALOYLMETHANE BY OZAWA METHOD

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Abstract

The lanthanidic complexes of general formula $Ln(C_{11}H_{19}O_2)_3$ were SYNThesized and characterized by elementary analysis, infrared absorption espectroscopy, thermogravimetry (TG) and differential scanning calorimetry (DSC). The reaction of thermal decomposition of complexes has been studied by non-isothermal and isothermal TG. The thermal decomposition reaction of complexes began in the solid phase for $Tb(thd)_3$, $Tm(thd)_3$ and $Yb(thd)_3$ and in the liquid phase for $Er(thd)_3$ and $Lu(thd)_3$, as it was observed by TG/DTG/DSC superimposed curves. The kinetic model that best adjusted the experimental isothermal thermogravimetric data was the R1 model. Through the Ozawa method it was possible to find coherent results in the kinetic parameters and according to the activation energy the following stability order was obtained:

$$Tb(thd)_3>Lu(thd)_3>Yb(thd)_3>Tm(thd)_3>Er(thd)_3$$

Keywords: dipivaloylmethane, kinetic, Ozawa

Introduction

Bidentate ligands based on β-diketones form complexes covering virtually every metal and metalloid element of the periodic table. This ability in coordinate is related to keto–enol tautomerism, where the enolate form is prone to complex the element by using both oxygen atoms displaying a chelate ring. This property is widely explored not only due to its academic interest but also because of many practical applications [1–2]. In this context, attention to thermochemistry of ligands and complexes has been progressively increased over the last three decades [3–8]. Consequently, there is more metal 2,4-pentadionate thermochemical data than for any other group of complexes containing metal–oxygen bonds. However, there is a lack of these data for lanthanide elements.

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1388–6150/2004/ $ 20.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

The chelates of general formulate $Ln(thd)_3$ are of considerable interest because they are the first examples of chelates of the rare earth that are thermally stable and are volatile at moderately low temperature.

The reaction of thermal decomposition of complexes has been studied by non-isothermal and isothermal thermogravimetry (TG). The Ozawa non-isothermal method determines the value of activation energy through several thermogravimetric curves obtained at different heating rates [9]. This method was used to obtain the kinetics parameters (activation energy, reaction order and pre-exponential factor) by the following equation:

$$\lg\phi=\lg\left[\frac{AE}{Rg(\alpha)}\right]-2.315-0.4567\frac{E}{RT} \tag{1}$$

where α – decomposed fraction, T – temperature, ϕ – heating rate, E – activation energy, A – pre-exponential factor and R – gas constant.

In this work the thermal behavior, the kinetic model of decomposition reaction by isothermal method and the kinetic parameters by Ozawa method in 2,2,6,6-tetramethyl-3,5-heptanedionates of elements of lanthanide series have been studied.

Experimental

All reagents used throughout the experiments were reagent grade and the solvents were purified by distillation. 2,2,6,6-tetramethyl-3,5-heptanedione from Aldrich was first distilled at reduced pressure and the liquid was stored in a dark glass flask.

Metal oxides Ln_2O_3 (Ln=Yb, Lu, Tm, Er and Tb) from Sigma were initially transformed into salts, by reacting with nitric acid for the chelate preparations. The prepared sodium salt of 2,2,6,6-tetramethyl-3,5-heptanedione was dissolved in a water–ethanol mixture and added to an aqueous solution containing $M(NO_3)_3{\cdot}yH_2O$ in a 3:1 proportion. The suspension was stirred for two hours and the volume reduced to half of its initial value under vacuum, when the solid compound started to settle. It was filtered and dried in vacuum for one hour, to give yields greater than 86% [10–12].

These compounds were purified through sublimation and submitted to carbon and hydrogen analysis using a Perkin Elmer 2400 CHN instrument.

Each sublimed chelate was treated with hydrochloric acid and the content of metal was determined by titration with standard EDTA solution [13].

Infrared spectra were recorded as KBr pellets in a Bomem MB-102 spectrophotometer and in the 4000 to 400 cm^{-1} interval.

The enthalpies of fusion of chelates were determined in a Shimadzu DSC-50 differential scanning calorimeter, heating rate of 10°C min^{-1}, purged with dry nitrogen and temperature interval 28–500°C.

Thermogravimetric curves were obtained using a Shimadzu TGA-50 thermobalance, heating rates of 5, 10 and 15°C min^{-1} in dynamic atmosphere of dry nitrogen, flux 50 mL min^{-1}, granulometry 200 mesh, mass 3.5±0.5 mg and temperature interval 28–500°C.

Results and discussion

The ligand 2,2,6,6-tetramethyl-3,5-heptadione presented a keto–enol tautomerism [1–2], where the enolate form has great ability in coordinate all lanthanide elements to give stable chelates of the general formula Ln(thd)$_3$. However, in the present case, results were restricted to compounds formed by *Ln* = Yb, Lu, Tm, Er and Tb. These air-sensitive chelates were always manipulated in atmosphere of dry nitrogen and have the metal, carbon and hydrogen analyzed after subliming in vacuum. The results were listed in Table 1. From the obtained content of the elements for this series, it was denoted that these values were within the experimental error of the expected results [10–12].

Table 1 Content of metal and elementary analysis of complexes

Complex	Metal/%		C/%		H/%	
	calc.	exp.	calc.	exp.	calc.	exp.
Tb(thd)$_3$	21.46	21.50	55.46	56.40	8.05	8.02
Tm(thd)$_3$	20.76	20.79	55.15	55.20	7.65	7.68
Lu(thd)$_3$	20.22	20.19	54.62	54.65	7.87	7.90
Er(thd)$_3$	21.43	21.52	55.30	54.30	7.96	7.81
Yb(thd)$_3$	22.23	22.21	54.84	53.45	7.89	7.93

The infrared spectra were very similar, presenting a set of common bands, which were mainly due to the enolate form of the chelate, in agreement with other publications [14, 15]. However, an important point to be considered was related to the 3500 to 3350 cm^{-1} region in the spectra. The absence of OH stretching frequency corroborated with the existence of anhydrous compounds.

The principal absorption bands indicated the coupling in sequence of three bands (Table 2).

Thermal analysis

The thermogravimetric curves presented similar profiles, with one single event of thermal decomposition attributed the decomposition of ligand (thd)$_3$ and presented residue attributed to the metal corresponding (Table 3).

Differential scanning calorimetry (DSC)

The thermal decomposition reaction of complexes began in the solid phase for Tb(thd)$_3$, Tm(thd)$_3$ and Yb(thd)$_3$ and in the liquid phase for Er(thd)$_3$ and Lu(thd)$_3$ as it can be observed by TG/DTG/DSC superimposed curves (Figs 1–2).

Table 2 Principal absorption bands observed in the infrared spectra

Complexes	Wavenumber/cm^{-1}	Attributions
$Tb(thd)_3$	1578(s)	ν(C⎓C)+ν(C⎓)
	1572(m)	combination
	1505(s)	ν(C⎓)+ν(C⎓C)
$Tm(thd)_3$	1570(s)	ν(C⎓C)+ν(C⎓)
	1541(m)	combination
	1505(s)	ν(C⎓)+ν(C⎓C)
$Lu(thd)_3$	1571(s)	ν(C⎓C)+ν(C⎓)
	1557(m)	combination
	1508(s)	ν(C⎓)+ν(C⎓C)
$Er(thd)_3$	1571(s)	ν(C⎓C)+ν(C⎓)
	1555(m)	combination
	1508(s)	ν(C⎓)+ν(C⎓C)
$Yb(thd)_3$	1571(s)	ν(C⎓C)+ν(C⎓)
	1556(m)	combination
	1506(s)	ν(C⎓)+ν(C⎓C)

(s) – strong intensity band; (m) – medium intensity band; (ν) – stretching.

Table 3 Thermogravimetric data of complexes

Complexes	Event	Temperature interval/°C	Mass loss/%	
			calc.	exp.
$Tb(thd)_3$	1	141.58–270.69	95.75	95.76
	residue	>270.69	4.25	4.24
$Tm(thd)_3$	1	140.93–259.39	88.49	88.62
	residue	>259.39	11.51	11.38
$Lu(thd)_3$	1	151.16–243.88	95.65	95.66
	residue	>243.88	4.34	4.34
$Er(thd)_3$	1	116.51–273.19	72.86	72.87
	residue	>273.19	27.13	27.13
$Yb(thd)_3$	1	141.24–257.30	98.42	98.43
	residue	>257.30	1.57	1.57

The principal transitions of complexes observed in the DSC indicated the fusion and vaporization temperatures and respective enthalpies (Table 4).

Table 4 Principal transitions observed in the complexes

Complexes	Melting temp./°C	Melting enthalpy/ kJ mol^{-1}	Vaporization temp./°C	Vaporization enthalpy/ kJ mol^{-1}
$Tb(thd)_3$	180	32.57	207	66.11
$Tm(thd)_3$	162	28.94	202	56.35
$Lu(thd)_3$	171	37.88	279	58.13
$Er(thd)_3$	173	30.72	229	51.31
$Yb(thd)_3$	163	32.57	207	54.36

Kinetic study

The kinetic model of decomposition reactions of complexes and its rate constant (k) was determined by isothermal method based in the different models of heterogeneous reactions, experimental data were treated for linear regression technical. For all complexes the kinetic model that best fitted the experimental curves was the one-

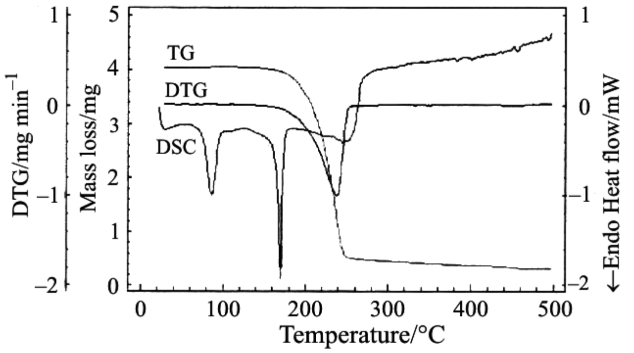

Fig. 1 TG/DTG/DSC superimposed curves of $Tm(thd)_3$ complex

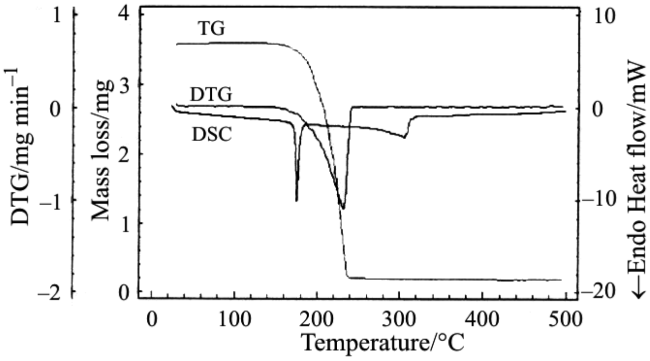

Fig. 2 TG/DTG/DSC superimposed curves of $Lu(thd)_3$ complex

dimensional phase-boundary controlled model (R1), in the interval of decomposed fraction (α) 0.10 to 0.90. The rate constant presented coherent values increasing in agreement with the increase of temperature (Table 5).

Table 5 Rate constant of thermal decomposition of complexes

Parameters	Tb isothermal temperature/°C				
	178	180	183	186	189
k/s^{-1}	2.651E-04	2.661E-04	4.009E-04	5.328E-04	5.763E-04
r	0.998	0.998	0.999	0.999	0.999
sd	1.175E-02	1.175E-02	5.684E-03	5.824E-03	5.297E-03
Parameters	Tm isothermal temperature/°C				
	152	156	158	160	162
k/s^{-1}	5.421E-05	7.442E-05	8.021E-05	9.248E-05	1.105E-04
r	0.996	0.999	0.998	0.998	0.997
sd	1.849E-02	6.708E-03	1.04E-02	1.169E-02	1.527E-02
Parameters	Lu isothermal temperature/°C				
	175	178	185	187	190
k/s^{-1}	2.688E-04	3.353E-04	7.160E-04	7.290E-04	8.667E-04
r	0.9975	0.9986	0.9996	0.9990	0.9993
sd	1.563E-02	1.118E-02	5.652E-03	9.756E-03	8.001E-03
Parameters	Er isothermal tempreature/°C				
	155	158	161	167	170
k/s^{-1}	4.3057E-05	5.6986E-05	7.2908E-05	1.1532E-04	1.4691E-04
r	0.9964	0.9991	0.9970	0.9990	0.9965
sd	1.8584E-02	9.0467E-03	1.6976E-02	9.6108E-03	1.7919E-02
Parameters	Yb isothermal temperature/°C				
	177	180	183	186	189
k/s^{-1}	3.621E-04	4.4473E-04	5.1538E-04	5.8122E-04	6.9497E-04
r	0.9988	0.9993	0.9987	0.9978	0.9987
sd	1.0589E-02	8.1615E-03	1.1218E-02	1.4521E-02	1.1213E-02

The kinetic parameters (reaction order, activation energy and pre-exponential factor) were determined by Ozawa method in the heating rates of 5, 10 and 15°C min^{-1} applied in the Shimadzu thermal analysis software. The results indicated medium values of kinetic parameters obtained by thermogravimetric data in the temperature interval refers at decomposition of complexes (Table 6).

Table 6 Kinetic parameters resulting of Ozawa method

Complexes	n	E/kJ mol^{-1}	A/s^{-1}
Tb(thd)$_3$	0.3	109.00	$3.2\cdot10^{12}$
Tm(thd)$_3$	0.2	89.97	$3.5\cdot10^{10}$
Lu(thd)$_3$	0.2	98.13	$3.9\cdot10^{11}$
Er(thd)$_3$	0.2	87.35	$2.0\cdot10^{10}$
Yb(thd)$_3$	0.3	92.39	$7.2\cdot10^{10}$

Conclusions

The profile of thermogravimetric curves was similar and presented one single event of thermal decomposition.

The thermal decomposition reaction of complexes began in the solid phase for Tb(thd)$_3$, Tm(thd)$_3$ and Yb(thd)$_3$ and in the liquid phase for Er(thd)$_3$ and Lu(thd)$_3$ as it was observed by TG/DTG/DSC superimposed curves.

The isothermal kinetic data indicated that the complexes adjusted better to the R1 kinetic model. The Ozawa non-isothermal method presented coherent results in the kinetic parameters and according the activation energy the following stability order was obtained:

$$\mathrm{Tb(thd)_3>Lu(thd)_3>Yb(thd)_3>Tm(thd)_3>Er(thd)_3}$$

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The authors acknowledge to CNPq and CAPES for financial support.

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