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KINETIC STUDY OF CHELATES OF 2,2,6,6-TETRAMETHYL-3,5-HEPTANEDIONE WITH SOME LANTHANIDE ELEMENTS

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Abstract

The thermal decomposition reactions of crystalline chelates of general formula Ln(thd)$_3$ (*Ln*=La, Pr, Nd, Sm and Gd; *thd*=2,2,6,6-tetramethyl-3,5-heptanedione) have been studied by isothermal thermogravimetry. Several models were proposed initially to calculate the kinetic parameters by isothermal method, thus the time reduced method was used to define the best kinetic models. The Avrami–Erofeev (*Am*=2, 3 and 4) and R1 and R2 models presented good agreement with experimental data, as well as, linear correlation coefficient (r) and standard deviation (s).

Keywords: kinetic analysis, lanthanide, 2,2,6,6-tetramethyl-3,5-heptanodione, thermal decomposition, thermogravimetry

Introduction

During the characterization of compounds by using some thermal behaviours, ligand exchange reactions have been explored in attempting to follow the thermal stability of chelates, such as those of general formula Ln(thd)$_3$. From the point of view of structural elucidations a large number of techniques have been employed and as expected for all other β-diketonates, both oxygen atoms coordinate the lanthanide cation in a bidentate way [1]. A special elucidation involving these chelates is devoted to the vapor pressure of the triad M(thd)$_3$ (*M*=Cu, Y and Ba), mainly due to their application in gas-phase thermolysis for production of high superconducting films and coatings. In such an operation these chelates can be used as initial components in this specific technology [2].

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The thermal stability properties of lanthanide chelates have been previously explored, without focusing on kinetic behavior. Here, some data related to the kinetic analysis of the thermal decomposition of 2,2,6,6-tetramethyl-3,5-heptanedione chelates of lanthanum, praseodymium, neodymium and gadolinium elements are now reported.

Experimental

Metal oxides M_2O_3 (M=La, Pr, Nd, Sm, Gd) from Sigma were initially transformed into salts, by reacting with nitric acid for 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 [3].

The melting temperatures for all compounds were determined by means of a Microquímica model MQAPF-301 apparatus. Infrared spectra were recorded with KBr pellets and Nujol mulls on a Bomem, model MB–102 spectrophotometer. The enthalpies of fusion of the chelates were determined in a Shimadzu model DSC-50 differential scanning calorimeter, at a heating rate of 10°C min^{-1}, purged with dry nitrogen with flux of 0.83 mL s^{-1}. Thermogravimetric curves were obtained using a Shimadzu model TGA-50 thermobalance, at a heating rate of 10°C min^{-1} in a dynamic atmosphere of dry nitrogen with flux of 0.83 mL s^{-1} and with granulometric control of 200 tyler and mass of the samples of 3.5±0.5 mg. X-ray Siemens model D-5000 Diffractor was used for residue analysis after thermal decomposition.

Results and discussion

The ligand 2,2,6,6-tetramethyl-3,5-heptadione (Hthd) presents a keto–enol tautomerism [1], presenting the enolate form (*thd*) with great ability in coordinating all lanthanide elements, to give stable chelates of the general formula $Ln(thd)_3$ [4]. However, in the present case, results are restricted to compounds for Ln=La, Pr, Nd, Sm, Gd. These air-sensitive chelates were always manipulated in an atmosphere of dry nitrogen and have the metal, carbon and hydrogen analyzed, after subliming in vacuum, Table 1. From the obtained contents of the elements for these chelates, the observed values are within the experimental error of the expected results of the established empirical formula. The melting temperatures are in good agreement with those reported [3], Table 1. The infrared spectra in the 4000 to 400 cm^{-1} range are very similar, presenting a set of common bands, which are mainly due to the enolate form of the chelate, indicating a complete agreement with published results [5].

Due to the similarity of these chelates, identical decomposition curves were observed in the thermogravimetric analysis for all compounds. However, as observed before, the temperature of the one-step decomposition follows the inverse of the radius of the cation of the trivalent lanthanide. In all cases, calculations indicated that the final decomposition leaves only the oxide as residue, which results were also supported by X-ray analysis. The thermogravimetric curves obtained indicate the follow the thermal stability order: $La(thd)_3>Pr(thd)_3>Nd(thd)_3>Sm(thd)_3>Gd(thd)_3$. Superimposed curves of TG/DTG/DSC show that in all the obtained chelates, the thermal decomposition starts at lower temperature than its melting temperature.

Table 1 Mass percentage calculated (found) analysis and melting temperature (T_M) of the chelates Ln(thd)$_3$

Ln(thd)$_3$	Ln	C	H	T_M/°C
La	20.23(20.19±0.02)	57.55(57.14±0.07)	8.34(8.54±0.02)	257
Pr	20.40(20.44±0.03)	57.38(56.06±0.06)	8.32(8.34±0.02)	219
Nd	20.78(20.80±0.02)	57.11(57.02±0.04)	8.28(8.30±0.04)	216
Sm	21.47(21.52±0.19)	56.61(56.83±0.09)	8.21(8.32±0.03)	195
Gd	22.24(22.23±0.02)	56.06(56.91±0.07)	8.13(8.29±0.03)	170

The application of the isothermal method in the thermal decomposition investigation of the reactions of chelates gives the way to identify the mechanism by which the reactions are processed, as well as to determine the kinetic parameters: apparent activation energy (*E*) and frequency factor (*A*). The choice of the temperature to adapt the accomplishment of the experiment was adjusted with the help of the dynamic TG curves, by considering the heating rate of 10°C min^{-1}, which results are shown in the Table 2.

The identification of the mechanism of reactions adapted for the chelates were based on different models of heterogeneous reactions in the solid state [6–9], the results are listed in Table 2.

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

Model	Parameters	Isothermal temperature/°C				
La(thd)$_3$		215	221	227	233	239
A2	k/s^{-1}	1.20E-04	1.92E-04	2.73E-04	4.24E-04	6.25E-04
	r	0.9980	0.9911	0.9904	0.9915	0.9928
	s	2.13E-02	4.76E-02	4.87E-02	4.53E-02	4.53E-02
A3	k/s^{-1}	7.88E-05	1.30E-04	1.86E-04	2.88E-04	4.36E-04
	r	0.9996	0.9968	0.9964	0.9967	0.9973
	s	6.19E-03	1.92E-03	2.00E-02	1.89E-02	1.93E-02
A4	k/s^{-1}	5.89E-05	9.90E-05	1.41E-04	2.19E-04	3.36E-04
	r	0.9994	0.9982	0.9980	0.9979	0.9973
	s	5.86E-03	1.08E-02	1.13E-02	1.16E-02	1.49E-02
Pr(thd)$_3$		206	209	212	215	218
A2	k/s^{-1}	2.82E-04	3.26E-04	4.22E-04	5.40E-04	6.94E-04
	r	0.9949	0.9920	0.9910	0.9955	0.9928
	s	3.60E-02	4.44E-02	4.37E-02	3.29E-02	4.31E-02
A3	k/s^{-1}	1.90E-04	2.21E-04	2.86E-04	3.67E-04	4.69E-04
	r	0.9983	0.9971	0.9964	0.9983	0.9977
	s	1.37E-02	1.82E-02	2.00E-02	1.38E-02	1.65E-02

Table 2 Continued

Model	Parameters	Isothermal temperature/°C				
$Pr(thd)_3$		206	209	212	215	218
A4	k/s^{-1}	1.44E-04	1.67E-04	2.17E-04	2.79E-04	3.55E-04
	r	0.9986	0.9981	0.9977	0.9982	0.9986
	s	9.37E-03	1.11E-02	1.22E-02	1.08E-02	9.58E-03
$Nd(thd)_3$		200	203	207	212	215
A2	k/s^{-1}	1.86E-04	2.34E-04	3.36E-04	4.73E-04	5.97E-04
	r	0.9990	0.9922	0.9969	0.9992	0.9941
	s	1.67E-02	4.37E-02	2.87E-02	1.41E-02	3.83E-02
A3	k/s^{-1}	1.25E-04	1.59E-04	2.25E-04	3.16E-04	4.03E-04
	r	0.9995	0.9973	0.9994	0.9988	0.9981
	s	7.96E-03	1.73E-02	8.24E-03	1.20E-02	1.45E-02
A4	k/s^{-1}	9.40E-05	1.21E-04	1.70E-04	2.39E-04	3.05E-04
	r	0.9984	0.9984	0.9993	0.9972	0.9987
	s	1.06E-02	1.00E-02	7.00E-03	1.40E-02	9.06E-03
$Sm(thd)_3$		185	187	190	193	195
A2	k/s^{-1}	2.02E-04	2.36E-04	3.06E-04	4.05E-04	4.67E-04
	r	0.9959	0.9973	0.9969	0.9978	0.9921
	s	3.29E-02	2.73E-02	2.91E-02	2.60E-02	4.45E-02
A3	k/s^{-1}	1.36E-04	1.59E-04	2.06E-04	2.68E-04	3.17E-04
	r	0.9990	0.9995	0.9994	0.9994	0.9971
	s	1.07E-02	7.63E-03	8.34E-03	9.03E-03	1.81E-02
$Gd(thd)_3$		163	165	167	168	170
R2	k/s^{-1}	3.16E-05	5.77E-05	9.03E-05	1.01E-04	1.14E-04
	r	0.9999	0.9998	0.9987	0.9991	0.9995
	s	2.20E-03	3.97E-03	1.03E-02	8.70E-03	6.48E-03
R3	k/s^{-1}	2.60E-05	4.71E-05	7.32E-05	8.21E-05	9.31E-05
	r	0.9986	0.9972	0.9944	0.9951	0.9968
	s	8.93E-03	1.25E-02	1.74E-02	1.62E-02	1.37E-02
A2	k/s^{-1}	5.66E-05	1.03E-04	1.62E-04	1.80E-04	2.04E-04
	r	0.9996	0.9991	0.9979	0.9980	0.9991
	s	1.08E-02	1.57E-02	2.35E-02	2.28E-02	1.60E-02

The experimental data were treated by linear regression technique using the relationship $g(\alpha)=kt+k_0$. Adjustments were employed for values of the decomposed function (α) superior to 0.15 due to TG curves, which did not present isothermal characteristics at the beginning, in order to attenuate the incidence of mistakes. For this operation interval $0.15<\alpha<0.95$ of α was used. Since several models were applied, as presented in Table 2, the reduced time method [10, 11] was used to define the best model that represents the processes.

Velocity constant (k), linear correlation coefficient (r) and standard deviation (s) between theoretical and experimental curves of the chelates were obtained through these models and the results are listed in the Table 2. The following best models were selected from the theoretically constructed curves: (A2, A3 and A4) for La(thd)$_3$, Pr(thd)$_3$ and Nd(thd)$_3$, respectively, (A2 and A3) for Sm(thd)$_3$ and (A2, R2 and R3) for Gd(thd)$_3$.

After determining the kinetic model that best describes the reaction the kinetic parameters; the activation energy (*E*) and the frequency factor (*A*) were calculated through the linearized form of Arrhenius equation [12]. The linear correlation coefficients (*r*) and standard deviation (*s*), were calculated and listed in Table 3.

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

Chelate	Parameter	Mechanism		
		A2	A3	A4
La(thd)$_3$	A/s^{-1}	$1.824\cdot10^{11}$	$2.874\cdot10^{11}$	$4.470\cdot10^{11}$
	E/kJ mol^{-1}	141.79	145.33	148.28
	r	0.9995	0.9979	0.9990
	s	0.0248	0.0499	0.0353
		A2	A3	A4
Pr(thd)$_3$	A/s^{-1}	1.364E+13	1.037E+13	8.153E+12
	E/kJ mol^{-1}	153.20	153.68	153.82
	r	0.9677	0.9688	0.9692
	s	0.1066	0.1050	0.1044
		A2	A3	A4
Nd(thd)$_3$	A/s^{-1}	5.268E+12	2.234E+13	1.665E+13
	E/kJ mol^{-1}	148.95	156.44	156.38
	r	0.9995	0.9982	0.9978
	s	0.0176	0.0330	0.0368
		A2	A3	–
Sm(thd)$_3$	A/s^{-1}	1.927E+17	0.189E+17	–
	E/kJ mol^{-1}	184.38	183.99	–
	r	0.9941	0.9955	–
	s	0.0005	0.0003	–
		A2	R2	R3
Gd(thd)$_3$	A/s^{-1}	3.807E+31	6.801E+39	4.308E+39
	E/kJ mol^{-1}	298.55	370.22	369.29
	r	0.9557	0.9671	0.9690
	s	0.1782	0.1541	0.1491

Linear correlation coefficients (*r*), standard deviation (*s*)

As can be observed in Table 3, the activation energy decreases with the increasing radius of the metallic cation and with thermal stability, independently of the reaction mechanism. Furthermore, correlations were observed among the activation energy with the parameters: metal ionic radii, temperature on set or atomic number. The behaviours similar to the correlations show linear sequence for metals La, Nd, Pr and

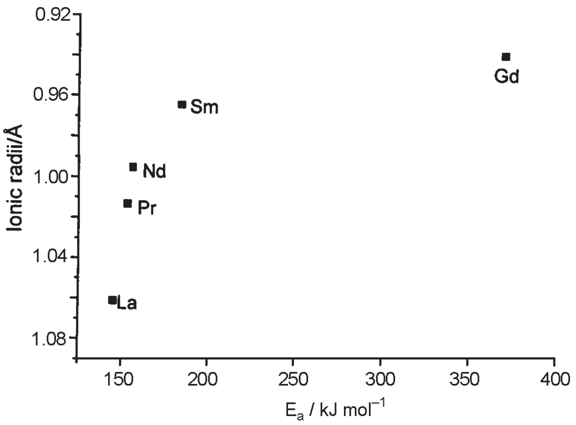

Fig. 1 Correlations of the activation energy (*E*) *vs*. metal ionic radii

Sm, as illustrated in Fig. 1. However, this linearity is not observed for gadolinium chelate, which should be related with the energy of the electronic configuration [13].

Conclusions

The best kinetic models are in agreement with the experimental results of isothermal method for Ln(thd)$_3$ chelates were: A_2, A_3, A_4, R_1, R_2 and R_3 models. The method of reduced time used to define the best reaction mechanism was not satisfactory, due to the fact that it did not define a unique decomposition mechanism for the chelate, but reducing from six to three. The following best models were: (A_2, A_3 and A_4) for La(thd)$_3$, Pr(thd)$_3$ and Nd(thd)$_3$; (A2 and A3) for Sm(thd)$_3$ and (A_2, R_2 and R_3) for Gd(thd)$_3$. The activation energy decreases with the increasing radius of the metallic cation and with thermal stability, independently of the mechanism of reaction.

The lanthanide elements present similar properties, however, Gd(thd)$_3$ chelate presented different results in relation to other, due to the electronic configuration of Gd^{3+} [(Xe)4f^7], enabling the 4f sub-level electrons disposed in a semi filled shell, giving a favourable energetic state.

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