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Kinetic Studies on Thermal Decomposition of Mixed Ligand Complexes of Lanthanide(III) Ions

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Some mixed ligand complexes of lanthanide(III) ions with 4-hydroxy-3′,4-dimethoxy diphenyl azomethine (HDDA) and diphenyl sulfoxide (DPSO) and various coordinating anions such as nitrate, perchlorate and thiocyanate have been synthesized and their kinetics on thermal decomposition were studied. The activation energies for the decomposition stages were calculated by Coats-Redfern and Madhusoodhanan-Krishan-Ninan equations. The tentative mechanism for the thermal decomposition has been proposed.

Key Words: Kinetic, Thermal, Decomposition, Lanthanide, Complexes.

INTRODUCTION

The pharmaceutical and industrial applications of lanthanide chelates[1] attracted a number of researchers to investigate their kinetics and thermal stability. The kinetics on thermal decomposition of metal chelates with azomethine ligands have been carried out by a number of workers[2–4]. However, little information is available on the kinetics of metal complexes of mixed ligands. Therefore it was considered worthwhile to investigate the kinetics of mixed ligand complexes of lanthanide(III) ions.

EXPERIMENTAL

The synthesis and characterization of the mixed ligand complexes of 4-hydroxy-3′,4-dimethoxy diphenyl azomethine (HDDA) and diphenyl sulfoxide (DPSO) with the lanthanide metal ions, *viz*., Pr(III), Nd(III), Dy(III), Eu(III) and Gd(III) in presence of the coordinating anions, *viz*., nitrate, perchlorate and thiocyanate were reported[5]. These complexes were reported[6] to have appreciable antibacterial activities. In continuation of our research work with these complexes we have tried to investigate the kinetic aspects of these complexes. The nitrato and thiocyanato complexes Pr(III), Nd(III), Dy(III) and Gd(III) with HDDA and DPSO were assigned the composition as $[Ln(HDDA)_2(DPSO)(NO_3)_3]$ and $[Ln(HDDA)_2(DPSO)(NCS)_3]$ whereas the perchlorato complex of Eu(III) as $[Eu(HDDA)_3(DPSO)(ClO_4)_2]ClO_4$ with a coordination number of six.

Thermal analysis was carried out using a Perkin-Elmer 7 series thermal analysis system. A constant heating rate of 10°C min^{-1} and a sample mass of about 5 mg were employed for the entire study. The fractional decomposition (α) was determined directly form the TG curves.

Evaluation of reaction mechanism from non-isothermal methods has been

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described by Sestak and Berggren[7] and Satava[8]. In the present study the mechanism based equations proposed by Satava have been used. The procedure is based on the assumption that the non-isothermal reaction proceeds isothermally in an infinitesimal time interval, so that the rate can be expressed by an Arrhenius type equation.

$$\frac{d\alpha}{dt} = Ae^{-E/RT}f(\alpha) \qquad (1)$$

where A is pre-exponential factor and f(α) depends on the mechanism of the process. For a linear rate ϕ (dT/dt = ϕ), on substitution and rearranging eqn. (1), becomes

$$\frac{d\alpha}{f(\alpha)} = \frac{A}{\phi}\,\theta^{-E/RT}\,dT \qquad (2)$$

Integration of eqn. (2) gives

$$\int_0^{\alpha} \frac{d\alpha}{f(\alpha)} = g(\alpha) = \frac{A}{\phi}\int_0^{T} e^{-E/RT}\,dT \qquad (3)$$

where g(α) is the integrated form of f(α). A series of f(α) is proposed and the mechanism is obtained from that which gives the best representation of the experimental data. A plot of log g(α) *vs.* 1/T will give a straight line provided the mechanism is correct. So, nine mechanistic equations proposed by Satava[8] can be used to draw the log g(α) *vs.* 1/T plots. The form of g(α) which best represents the experimental data gives the proper mechanism of the reaction[7]. Depending on the integrated form of the temperature integral, the plots may be $\log[g(\alpha)/T^2]$/*vs.* 1/T or log g(α) *vs.* 1/T. Using computer, linear plots were drawn for the nine forms of $[g(\alpha)/T^2]$ *vs.* 1/t by the method of least squares and the reaction mechanism was chosen from the best linear curve.

Several authors have adopted different methods for the evaluation of reaction mechanism from non-isothermal kinetic data. The major difficulty in non-isothermal method is that more than one equation gives good linear curves with high correlation coefficient, so that it may become difficult to assign the reaction mechanism unequivocally from the linearity of the curve alone. In the present work the method described by Ninan *et al.*[9] was employed in which the reaction mechanism was selected through statistical analysis and on the basis of the best linear fit (maximum correlation coefficient and least residual) for the appropriate $\log[g(\alpha)/T^2]$ *vs.* 1/t plots.

Kinetic parameters are calculated from two non-mechanistic equations. The forms of these equations used are given below wherein the integrated form of g(α) has been introduced for convenience and is defined as

$$g(\alpha) = \frac{1-(1-\alpha)^{1-n}}{1-n}$$

where α = the fractional decomposition at t related to the sample mass from TG as m_0/m_α and *n* = order parameter.

Coats-Redfern equation:

$$\ln\left[\frac{g(\alpha)}{T^2}\right] = \ln\left[\frac{AR}{\phi E}\left(1-\frac{2RT}{E}\right) - \frac{E}{RT}\right]$$

MKN equation:

$$\ln\left[\frac{g(\alpha)}{T^{1.9215}}\right] = \ln\left[\frac{AE}{\phi R}\right] + 3.7721 - 1.9215 \ln E \frac{-0.12039E}{T}$$

where T is the temperature (K), A is the preexponential factor, ϕ is the heating rate (°C min^{-1}), E is the energy of activation, R is the gas constant.

The order parameters were evaluated for the different stages of decomposition using the Coats-Redfern equation by an iteration method. Using a computer, linear plots of ln $[g(\alpha)/T^2]$ *vs.* 1/T were drawn by the method of least squares. Linear curves were drawn for different values of n ranging from 0 to 2, in increments of 0.1. The value of n which gave the best fit was chosen as the order parameter for each stage of decomposition.

RESULTS AND DISCUSSION

The complexes were subjected to thermal study in an atmosphere of oxygen. Each complex has two stages of decomposition. The first one represents the decomposition of the secondary ligand DPSO from the complex followed by the formation of the oxide. The thermal behaviour of the complexes including stability ranges, peak temperatures and weight loss data are presented in Table-1. It can be seen that for all the complexes for the two stages of decomposition the order parameter obtained was a value ranging from 0.8 to 1.3.

The kinetic parameters evaluated for the different stages of decomposition, using the two non-mechanistic equations, *viz.*, Coats-Redfern and MKN, are listed in Table-2. The correlation coefficients were in the range 0.99602–0.9966 indicating nearly perfect fits.

The decomposition stages with positive value of ΔS indicate that the activated complex has a less ordered structure as compared to the reactant and the reaction in these cases may be described as faster than normal[10]. The stages having negative value of entropy of activation indicate that the activated complex has a more ordered structure than the reactant and the reaction is slower than normal.

TABLE-1
TG-DTG DATA OF LANTHANIDE(III) COMPLEXES OF SCHIFF BASE AND DIPHENYL SULPHOXIDE

Complex	DTG (K)				Final residue	Percentage mass of final product	
	First stage	Peak temp.	Second stage	Peak temp.		Independent pyrolysis	Theoretical
$[Pr(HDDA)_2(DPSO)(NO_3)_3]$	433–613	510	723–803	756	Pr_6O_{11}	16.31	16.33
$[Nd(HDDA)_2(DPSO)(NO_3)_3]$	413–573	517	613–713	663	Nd_2O_3	15.99	16.06
$[Dy(HDDA)_2(DPSO)(NO_3)_3]$	413–533	453	573–673	644	Dy_2O_3	17.49	17.52
$[Eu(HDDA)_3(DPSO)(ClO_4)_2]ClO_4$	453–653	530	693–793	745	Eu_2O_3	12.31	12.36
$[Gd(HDDA)_2(DPSO)(NCS)_3]$	403–613	495	753–833	791	Gd_2O_3	17.28	17.31

TABLE-2
KINETIC PARAMETERS FOR THE DECOMPISITION OF VARIOUS LANTHANIDE (III) COMPLEXES WITH SCHIFF BASES AND DIPHENYL SULPHOXIDES USING TWO NON-MECHANISTIC EQUATIONS

Complex	Stage	n		E (kJ mol^{-1})	A (s^{-1})	ΔS (J K^{-1} mol^{-1})	r
Pr(HDDA)$_2$(DPSO)(NO$_3$)$_3$]	I	1	CR	33.878	1.453×10^{4}	–169.689	0.99869
			MKN	34.182	1.818×10^{4}	–167.825	0.99871
	II	1.1	CR	324.215	5.672×10^{23}	202.090	0.99947
			MKN	324.402	6.066×10^{23}	202.650	0.99947
[Nd(HDDA)$_2$(DPSO)(NO$_3$)$_3$]	I	0.8	CR	36.005	3.612×10^{4}	–162.232	0.99895
			MKN	36.288	4.462×10^{4}	–160.474	0.99897
	II	1.2	CR	139.163	4.776×10^{12}	–8.828	0.99827
			MKN	139.462	5.419×10^{12}	–7.778	0.99828
[Dy(HDDA)$_2$(DPSO)(NO$_3$)$_3$	I	1.1	CR	58.161	1.441×10^{7}	–111.341	0.99727
			MKN	58.412	1.704×10^{7}	–109.950	0.99730
	II	1.1	CR	165.992	2.240×10^{15}	42.550	0.99771
			MKN	166.239	2.486×10^{15}	43.410	0.99772
[Eu(HDDA)$_3$(DPSO)(ClO$_4$)$_2$]ClO$_4$	I	1.2	CR	56.934	2.642×10^{6}	–126.751	0.99850
			MKN	57.234	3.170×10^{6}	–125.236	0.99851
	II	1.1	CR	198.493	2.637×10^{15}	42.696	0.99798
			MKN	198.787	2.926×10^{15}	43.560	0.99799
Gd(HDDA)$_2$(DPSO)(NCS)$_3$]	I	1.0	CR	50.763	1.091×10^{6}	–133.536	0.99705
			MKN	51.039	1.314×10^{6}	–131.992	0.99708
	II	1.1	CR	313.860	1.285×10^{22}	170.227	0.99898
			MKN	314.576	1.385×10^{22}	170.848	0.99898

From calculation it can be seen that the highest correlation coefficient and the best fit curve is obtained from Mampel equation. Thus it can be concluded that the rate controlling process for the decomposition of these complexes follows a random nucleation mechanism with one nucleus on each particle.

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