Thermal Decomposition Kinetics and Mechanism of Lanthanide Nitrato Complexes of Pyridine-2-carboxaldehyde-4-aminoantipyrine and Dimethylsulfoxide

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The thermal decomposition behaviour of lanthanide nitrato complexes of the Schiff base, pyridine-2-carboxaldehyde-4-amino-antipyrine (P₂CA4AAP) and dimethylsulfoxide (DMSO), has been studied using TG and DTG analyses. The phenomenological and kinetic aspects of the TG curves are investigated for the evaluation of kinetic parameters such as activation energy, pre-exponential factor and entropy of activation using the Coats-Redfern equation. The rate controlling process obeys the 'Mampel model', representing random nucleation with one nucleus on each particle. There is no regular variation in the values of kinetic parameters for the decomposition of these complexes. The kinetic parameters indicate that the ligand is loosely bound to the metal ion and the activated complex is more ordered than the reactants.

Key Words: Kinetics, Thermal, Lanthanide(III) Complexes, Pyridine-2-carboxaldehyde-4-aminoantipyrine, Dimethylsulfoxide.

INTRODUCTION

Studies on the thermal decomposition and kinetics of metal chelates with Schiff bases have been measured by several workers[1, 2]. Wendlandt[3–5] and Hill[6, 7] studied the thermal properties of metal chelates with different types of complexing ligands. Nair and Radhakrishnan studied the thermal decomposition of various anion complexes of lanthanum with the Schiff base, 4-N-(4′-antipyrylmethyli-dene)aminoantipyrine[8] and 4-N-(4′-antipyrilmethylidene)aminoantipyrine[9]. The present investigation is concerned with the thermal decomposition behaviour of the lanthanide nitrato complexes of the Schiff base pyridine-2-carboxaldehyde-4-aminoantipyrine (P₂CA4AAP) and dimethylsulfoxide (DMSO).

EXPERIMENTAL

The Schiff base and complexes of lanthanide nitrates were prepared as reported earlier[10]. Thermogravimetric analyses were carried out on Shimadzu DT-40 and DuPont 2000 thermal analyzers in an atmosphere of nitrogen (sample mass *ca.* 5 mg; heating rate *ca.* 20 K min^{-1}).

RESULTS AND DISCUSSION

The complexes were characterized by metal and anion estimation, molecular mass determination, elemental analyses, magnetic susceptibility, conductance measurement in acetonitrile, methanol and nitrobenzene, infrared and electronic spectral studies. The complexes had the following general formula: [Ln(P$_2$CA4AAP)(DMSO)(NO$_3$)$_3$], where Ln = La, Nd and Gd. The Schiff base P$_2$CA4AAP acts as a neutral bidentate ligand, coordinating by carbonyl oxygen and the azomethine nitrogen, giving a five-membered ring system. DMSO coordinates unidentately with the lanthanide ions through the oxygen atom of the sulfoxide group of DMSO. Thus each of the lanthanide(III) ions in these complexes has a coordination number 6. These complexes show a two-stage decomposition (Figs. 1–3).
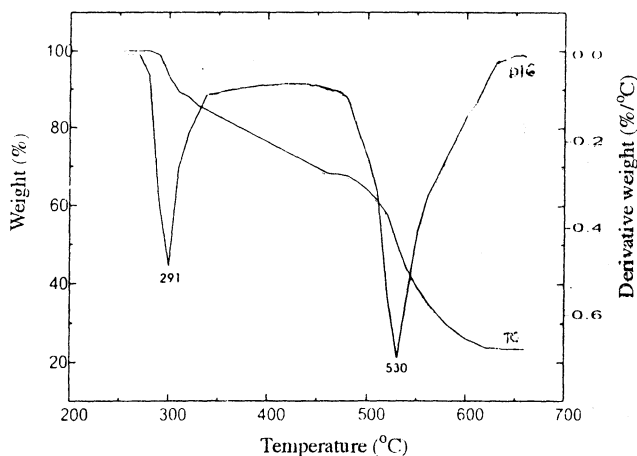

Fig. 1.   TG and DTG curves of [La(P$_2$CA4AAP)(DMSO)(NO$_3$)$_3$]
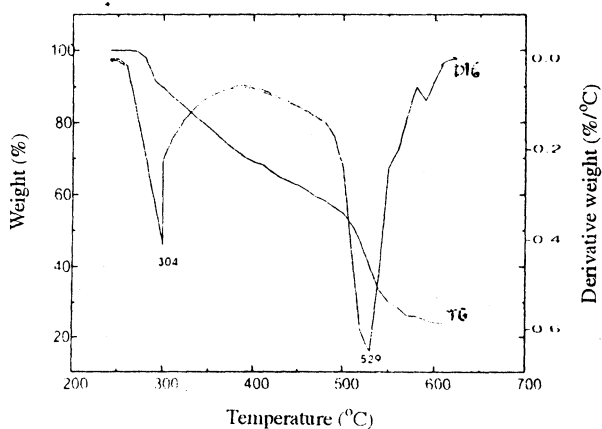
Fig. 2.   TG and DTG curves of [Nd(P$_2$CA4AAP)(DMSO)(NO$_3$)$_3$]
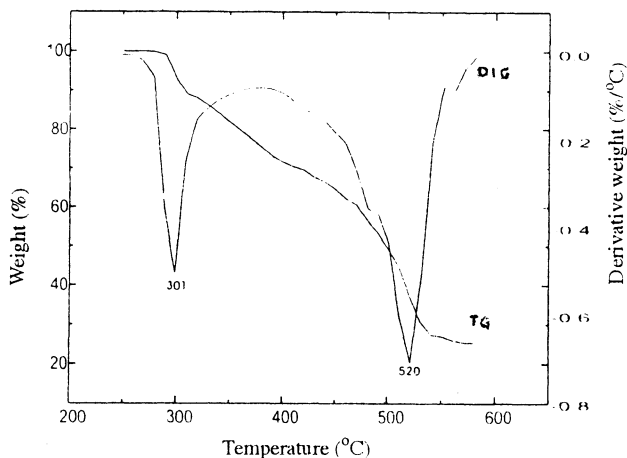
Fig. 3.   TG and DTG curves of [Gd(P$_2$CA4AAP)(DMSO)(NO$_3$)$_3$]

The lanthanum-nitrato complex [La(P$_2$CA4AAP)(DMSO)(NO$_3$)$_3$] is thermally stable up to *ca.* 250°C and undergoes decomposition in two stages (Table-1) in the range 250–330 and 480–620°C as indicated by the DTG peaks at 291 and 530°C.

TABLE-1

THE THERMAL DECOMPOSITION DATA OF NITRATO COMPLEXES OF LANTHANIDES WITH P$_2$CA4AAP AND DMSO

Complexes	TG plateaux (°C)	DTG peaks (°C)	DTG peak widths (°C)	Final residue at 700°C	Mass loss		
					Final TG (%)	Independent pyrolysis	Theoretical
[La(L)(DMSO)(NO$_3$)$_3$]	Upto 250 above 620	291 530	250–330 480–620	La$_2$O$_3$	24.0	23.3	23.43
[Nd(L)(DMSO)(NO$_3$)$_3$]	Upto 250 above 610	304 529	260–320 420–610	Nd$_2$O$_3$	24.5	23.9	24.01
[Gd(L)(DMSO)(NO$_3$)$_3$]	Upto 270 above 600	301 520	270–310 440–580	Gd$_2$O$_3$	25.5	25.2	25.39

The neodyminum-nitrato complex [Nd(P$_2$CA4AAP)(DMSO)(NO$_3$)$_3$] is stable up to *ca.* 260°C and undergoes decomposition in two stages in the range 260–320 and 420–610°C as indicated by the DTG peaks at 304 and 529°C.

The gadolinium-nitrato complex [Gd(P$_2$CA4AAP)(DMSO)(NO$_3$)$_3$] is stable up to *ca.* 270°C and undergo decomposition in two stages in the range 270–310 and 440–580°C as indicated by the DTG peaks at 301 and 520°C.

These complexes are thermally stable up to *ca.* 250°C. The first stage of decomposition amounts to a mass loss of *ca.* 11%, which may be attributed to the loss of a DMSO molecule and the second stage of decomposition amounts to a mass

loss of *ca.* 42%, which may be attributed to the loss of the ligand P$_2$CA4AAP molecule.

The final plateau occurs above 650°C after which there is no mass loss in the TG curve. The final residue obtained in each of the case is found to be La$_2$O$_3$, Nd$_2$O$_3$ and Gd$_2$O$_3$, which is in conformity with the mass loss data obtained from TG curve, independent pyrolysis and theoretical value.

The complexes show the same decomposition pattern suggests the same structure for all these complexes. The nitrato complexes of the lanthanides with P$_2$CA4AAP and DMSO are stable in the order La < Nd < Gd which may be attributed to decrease in size.

Kinetic Aspect

The kinetic parameters of the thermal decomposition of complexes were evaluated using a computer programme. Stage II of La, Nd and Gd complexes were selected for the study of the kinetics of the decomposition of the complexes. In all the complexes, these stages include the decomposition of the ligand part. The Coats-Redfern equation was used for calculating the kinetic parameters such as the activation energy (E) and the pre-exponential factor (A). The equation is:

$$\log \frac{g(\alpha)}{T^2} = \log \frac{AR}{\phi E} \frac{(1-2RT)}{E} - \frac{E}{2.303RT}$$

In the present work, log [g(α)/T^2] *vs.* 1000/T gave a straight line graph, whose slope and intercept are used for calculating the kinetic parameters by the least squares method. Evaluating the correlation coefficient tested the goodness of fit.

The entropy of activation (ΔS) can be calculated using the equation:

$$A = \frac{kTs}{h} e^{\Delta S/R},$$

where 'k' is the Boltzmann's constant and 'h' the Planck's constant.

The kinetic equations, which govern the reaction mechanism, are based on the assumption that the form of g(α) depends on the reaction mechanism. In the present investigation, the nine forms of g(α) codified by Satava[12] have been used. The form of g(α) representing the best experimental data is considered as the mechanism of the reaction. The highest value of correlation coefficient was for g(α) = $-\ln(1-\alpha)$ which is the 'Mampel model', representing random nucleation mechanism with one nucleus on each particle.

The kinetic parameters of the thermal decomposition reactions of the complexes are given in Table-2. These values are useful in assigning the strength of the bond in the complexes. There is no regular variation in the values of kinetic parameters of thermal decomposition of the complexes. The activation energy of the decomposition stages varies in the range 123–181 kJ/mol. This value is very low and is comparable with the activation energy of the dehydration of hydrated salts[13, 14]. This indicates that the ligands are loosely bound to the central metal ion. The result is in conformity with the weak covalency in the metal-ligand bond on account of the non-participation of 4*f*-electrons in bonding. The energy of activation and the entropy of activation increases in the order La < Nd < Gd. The ΔS values are negative for all the complexes indicating that the activated complex has a more ordered structure than the reactants and that the reactions are slower than normal[15, 16].

TABLE-2

KINETIC PARAMETERS OF THE THERMAL DECOMPOSITION OF LANTHANIDE-NITRATO COMPLEXES OF $P_2CA4AAP$ AND DMSO USING COATS-REDFERN EQUATION

Complexes	Decom-position stage	Peak temp: (K)	Energy of activation E_a $(kJ \cdot mol^{-1})$	Arrhenius factor A (s^{-1})	Entropy of activation ΔS (mol^{-1})	Correlation coefficient r	Order n
[La(L)(DMSO)(NO$_3$)$_3$]	2	803	123.27	1.92×10^{13}	−305.12	0.99339	1.1
[Nd(L)(DMSO)(NO$_3$)$_3$]	2	802	132.42	3.17×10^6	−128.69	0.99492	1.0
[Gd(L)(DMSO)(NO$_3$)$_3$]	2	793	181.62	1.14×10^{10}	−60.48	0.99477	0.9

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