

THERMAL STUDIES ON LANTHANIDE NITRATE COMPLEXES OF 4-N-(2'-FURFURYLIDENE)AMINOANTIPYRINE

C. R. Vinodkumar¹, M. K. Muraleedharan Nair¹ and P. K. Radhakrishnan^{2}*

¹Department of Chemistry, Maharajas College, Ernakulam, Kerala-682 011

²School of Chemical Sciences, Mahatma Gandhi University, Kottayam, Kerala-686 560, India

(Received August 8, 1999)

Abstract

The kinetics and mechanism of thermal decomposition of nitrate complexes of lanthanides with the Schiff base 4-N-(2'-furfurylidene)aminoantipyrine (abbreviated as FAA) have been studied by TG and DTG techniques. The kinetic data for the first stage of decomposition were calculated using the Coats-Redfern equation. The rate-controlling process obeys Mampel model representing random nucleation, with one nucleus on each particle. It is observed that there is no gradation in the values of the kinetic parameters of decomposition of the complexes.

Keywords: complexes, lanthanide nitrate, 4-N-(2'-furfurylidene)aminoantipyrine, TG

Introduction

Very few systems have been reported for lanthanide metal complexes showing the correlation between the thermal stability of metal chelates and the structure of the lanthanide complexes [1, 2]. Major contribution in this field have been reported by Wendlandt [3–5] and Hill [6]. Thermal properties of chelating ligands with azomethine coordination have been done by Pardeshi and Bhobe [7, 8]. In continuation of our work on Schiff base metal complexes with lanthanides [9–11], we report the thermal decomposition kinetics and mechanism of lanthanide nitrate complexes of FAA (empirical formula: C₁₆H₁₅N₃O₂).

Experimental

The Schiff base [12] and the metal complexes with lanthanide nitrates were prepared by the reaction between metal nitrate and the Schiff base in ethyl acetate medium [13]. The complexes were characterised by elemental analyses, magnetic susceptibil-

* Author to whom all correspondence should be addressed.

ity as well as infrared, proton NMR and electronic spectral studies. These complexes had the following general formulae $[\text{Ln}(\text{FAA})(\text{NO}_3)_2]\text{NO}_3$, where $\text{Ln}=\text{La, Pr, Nd, Sm, Eu, Gd, Dy, Ho}$ and Er . A coordination number of seven is assigned to the metal in these complexes.

Apparatus

TG and DTG analyses were carried out on a DuPont 2000 thermal analyser in an atmosphere of nitrogen (sample mass: 10 mg; heating rate: 10 K min^{-1}).

Results and discussion

All these complexes undergo thermal decomposition in two stages and the thermal data is given below.

Phenomenological data

The complexes are thermally stable up to about 200°C (Figs 1–9). The first stage of thermal decomposition starts at about $200\text{--}220$ and ends in the range $330\text{--}360^\circ\text{C}$ (Table 1). This involves a mass loss of about 26% which corresponds to the decomposition of the nitrate. This result is supported by the absence of nitrate ion in the intermediate obtained at 360°C which was confirmed by infrared spectral analysis. The DTG peak of this stage is observed at about $290\text{--}325^\circ\text{C}$. The second stage starts around 360 and ends at about 900°C which involves the decomposition of the ligand moiety. The final residue obtained is the corresponding metal oxide. The fact that the TG curves of all these ten complexes are comparable, points to the similarity in the structure.

Kinetic data

The kinetic parameters and the mechanism of the thermal decomposition of the first stage of these complexes were obtained by using Coats-Redfern equation [14].

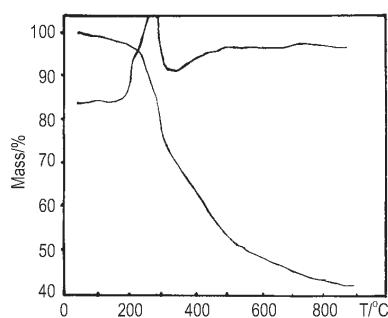


Fig. 1 TG and DTG curves of $[\text{La}(\text{FAA})(\text{NO}_3)_2]\text{NO}_3$ complex

$$\log\left[\frac{g(\alpha)}{T^2}\right]=\log\left(\frac{AR}{\Phi E}\left(1-\frac{2RT}{E}\right)\right)-\frac{E}{2.303RT}$$

where $\log g(\alpha)/T^2$ is plotted vs. $1000/T$ a straight line graph is obtained whose slope and intercept are used for calculating the activation energy (E) and the pre-exponential factor (A). The entropy of activation (ΔS) can also be calculated using the equation

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

The value of $g(\alpha)$, which represents nine forms of solid state mechanisms suggested by Satava [15], is selected by calculating the correlation coefficient. The value of $g(\alpha)$ with highest correlation coefficient is taken as the mechanism of thermal decomposition. Here, in the present study $g(\alpha)=-\ln(1-\alpha)$, which represent the Mampel model, is selected as the reaction mechanism in all the stages of decomposition which is random nucleation with one nucleus on each particle. The kinetic parameters of the thermal decomposition of these complexes were evaluated using a computer programme.

Table 1 Thermal decomposition data of lanthanide nitrate complexes of FAA

Complex	Decomposition range/ °C	DTA peak/	Mass loss obs. (calc.)/ %
[La(FAA)(NO ₃) ₂]NO ₃	200–330	315	26.20 (26.32)
[Pr(FAA)(NO ₃) ₂]NO ₃	200–342	295	26.50 (26.60)
[Nd(FAA)(NO ₃) ₂]NO ₃	210–360	320	27.00 (26.82)
[Sm(FAA)(NO ₃) ₂]NO ₃	215–350	315	26.00 (26.20)
[Eu(FAA)(NO ₃) ₂]NO ₃	200–330	290	25.50 (25.55)
[Gd(FAA)(NO ₃) ₂]NO ₃	215–345	320	26.89 (26.80)
[Dy(FAA)(NO ₃) ₂]NO ₃	220–340	320	26.10 (26.02)
[Ho(FAA)(NO ₃) ₂]NO ₃	215–340	310	26.25 (26.30)
[Er(FAA)(NO ₃) ₂]NO ₃	200–360	325	25.80 (25.79)

The kinetic parameters of the first stage of the thermal decomposition reaction of the lanthanide nitrates with FAA are given in Table 2. The activation energy for thermal decomposition varies from 84.84 to 132.25 kJ mol⁻¹ which indicates that the metal-ligand bond is very weak [15, 16]. The pre-exponential factor observed is in

the range 21.17 to $1.17 \cdot 10^3 \text{ s}^{-1}$. The entropy of activation varies from -191.79 to $-224.75 \text{ J mol}^{-1}$. There is no definite trend in the values of the energy of activation and entropy of activation. But the negative value of the entropy of activation indicates that the activated complex has a more ordered structure than the reactants [17, 18].

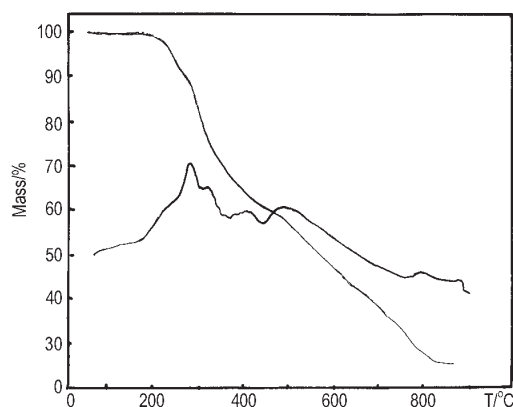


Fig. 2 TG and DTG curves of $[\text{Pr}(\text{FAA})(\text{NO}_3)_2]\text{NO}_3$ complex

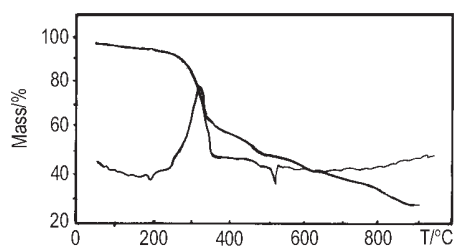


Fig. 3 TG and DTG curves of $[\text{Nd}(\text{FAA})(\text{NO}_3)_2]\text{NO}_3$ complex

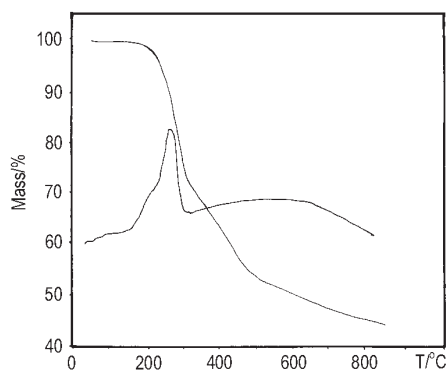


Fig. 4 TG and DTG curves of $[\text{Sm}(\text{FAA})(\text{NO}_3)_2]\text{NO}_3$ complex

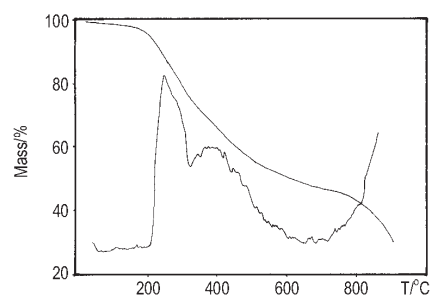


Fig. 5 TG and DTG curves of $[\text{Eu}(\text{FAA})(\text{NO}_3)_2]\text{NO}_3$ complex

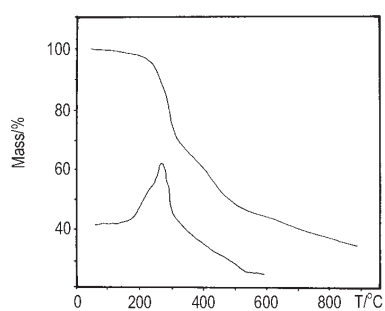


Fig. 6 TG and DTG curves of $[\text{Gd}(\text{FAA})(\text{NO}_3)_2]\text{NO}_3$ complex

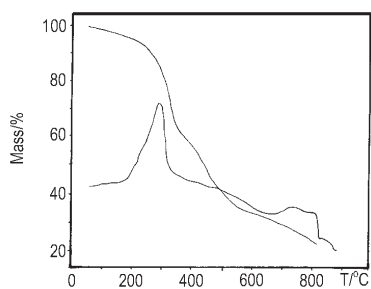


Fig. 7 TG and DTG curves of $[\text{Dy}(\text{FAA})(\text{NO}_3)_2]\text{NO}_3$ complex

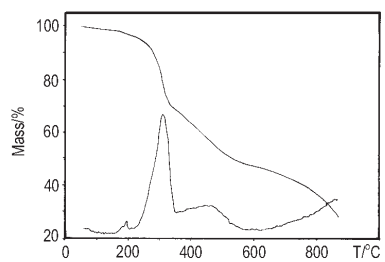


Fig. 8 TG and DTG curves of $[\text{Ho}(\text{FAA})(\text{NO}_3)_2]\text{NO}_3$ complex

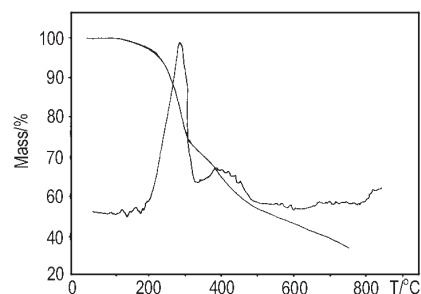


Fig. 9 TG and DTG curves of $[\text{Er}(\text{FAA})(\text{NO}_3)_2]\text{NO}_3$ complex

Table 2 Kinetic parameters of the thermal decomposition of lanthanide nitrate complexes of FAA

Complex	$E/\text{kJ mol}^{-1}$	A/s^{-1}	$\Delta S/\text{J mol}^{-1}$
$[\text{La}(\text{FAA})(\text{NO}_3)_2]\text{NO}_3$	98.61	64.83	-215.75
$[\text{Pr}(\text{FAA})(\text{NO}_3)_2]\text{NO}_3$	124.56	841.51	-194.49
$[\text{Nd}(\text{FAA})(\text{NO}_3)_2]\text{NO}_3$	132.25	1174.30	-191.79
$[\text{Sm}(\text{FAA})(\text{NO}_3)_2]\text{NO}_3$	112.58	210.65	-206.09
$[\text{Eu}(\text{FAA})(\text{NO}_3)_2]\text{NO}_3$	84.84	21.17	-224.75
$[\text{Gd}(\text{FAA})(\text{NO}_3)_2]\text{NO}_3$	101.16	67.30	-215.63
$[\text{Dy}(\text{FAA})(\text{NO}_3)_2]\text{NO}_3$	121.43	500.12	-198.96
$[\text{Ho}(\text{FAA})(\text{NO}_3)_2]\text{NO}_3$	127.99	1040.49	-192.74
$[\text{Er}(\text{FAA})(\text{NO}_3)_2]\text{NO}_3$	105.54	76.26	-214.85

* * *

The authors are grateful to Prof. P. M. Madhusudanan, for some helpful discussions. We are also grateful to the authorities of the University Grants Commission for granting a teacher fellowship to one among us (VK).

References

- 1 V. Indira and G. Parameswaran, *Thermochim. Acta*, 101 (1986) 145.
- 2 S. Laly and G. Parameswaran, *React. Kinet. Catal.*, 43 (1991) 169.
- 3 G. D. Ascenzo and W. W. Wendlandt, *J. Thermal Anal.*, 1 (1969) 423.
- 4 F. C. Chang and W. W. Wendlandt, *Thermochim. Acta*, 2 (1971) 293.
- 5 D. L. Perry, C. Vaz and W. W. Wendlandt, *Thermochim. Acta*, 9 (1974) 76.
- 6 C. G. Scency, J. F. Smith, J. O. Hill and R. J. Magce, *J. Thermal Anal.*, 9 (1976) 415.
- 7 L. Pardeshi and R. A. Bhobe, *Acta Cienc. Indica*, 8 (1982) 178.
- 8 L. Pardeshi and R. A. Bhobe, *Acta Cienc. Indica*, 9 (1983) 18.
- 9 M. K. Muraleedharan Nair and P. K. Radhakrishnan, *Thermochim. Acta*, 261 (1995) 141.
- 10 M. K. Muraleedharan Nair and P. K. Radhakrishnan, *Thermochim. Acta*, 292 (1997) 115.

- 11 M. K. Muraleedharan Nair and P. K. Radhakrishnan, *J. Therm. Anal. Cal.*, 52 (1998) 475.
- 12 C. R. Vinodkumar and P. K. Radhakrishnan, *Synth. React. Inorg. Met.-Org. Chem.*, 27 (1997) 1347.
- 13 C. R. Vinodkumar, Ph. D. Thesis, Mahatma Gandhi University, Kottayam, 1994.
- 14 A. W. Coats and J. P. Redfern, *Nature*, 210 (1964) 68.
- 15 T. Ganga Devi, K. Muraleedharan and M. P. Kannan, *Thermochim. Acta*, 191 (1991) 105.
- 16 M. Nath, *Thermochim. Acta*, 185 (1991) 11.
- 17 S. Mathew, C. G. R. Nair and K. N. Ninan, *Thermochim. Acta*, 144 (1989) 33.
- 18 K. K. Aravindakshan and K. Muraleedharan, *Thermochim. Acta*, 155 (1989) 247.