ELSEVIER

Thermochimica Acta 261 (1995) 141–149

thermochimica
acta

Kinetics and mechanism of the thermal decomposition of lanthanum complexes of 4-*N*-(4′-antipyrylmethylidene) aminoantipyrine

M.K. Muraleedharan Nair, P.K. Radhakrishnan *

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

Received 3 June 1994; accepted 19 February 1995

Abstract

The kinetics and mechanism of the thermal decomposition of perchlorate, nitrate, chloride, bromide, and iodide complexes of lanthanum with the Schiff base 4-*N*-(4′-antipyrylmethylidene) aminoantipyrine (abbreviated as AA) have been studied by TG and DTG techniques. The kinetic parameters for the major decomposition stages (stages I and II) were calculated using the Coats–Redfern equation. The rate-controlling process obeys Mampel's model with random nucleation, with one nucleus on each particle. It is observed that there is no regular variation in the values of the kinetic parameters of decomposition of the complexes as with other common physical constants, namely boiling point, melting point, etc.

Keywords: Coats–Redfern; Decomposition; Kinetics; Lanthanum complexes

1. Introduction

Wendlandt and co-workers [1–3] and Hill and co-workers [4, 5] have studied the thermal properties of metal chelates with different types of complexing ligands. The thermal decomposition and kinetics of metal chelates with Schiff bases have been studied by a few workers [6–9]. In the present communication we report our studies on the thermogravimetric analysis and the kinetics of the thermal decomposition of the perchlorate, nitrate, chloride, bromide, and iodide complexes of lanthanum with the Schiff base derived from antipyrine, namely, 4-*N*-(4′-antipyrylmethylidene)aminoantipyrine (empirical formula, $C_{23}H_{23}N_5O_2$).

---

* Corresponding author.

SSDI 0040-6031(95)02313-5

2. Experimental

The Schiff base and the complexes of lanthanum were prepared as reported earlier [10–13]. Thermogravimetric analyses were made on Shimadzu-DT-40 and DuPont 2000 thermal analysers in nitrogen atmosphere (sample mass, 10 mg; heating rate, 10°C min^{-1}).

3. Results and discussion

The elemental analysis, electrical conductance in non-aqueous media, magnetic moments, and infrared, electronic and proton NMR spectra show that the five complexes have the formulae: $[\mathrm{La(AA)_2(ClO_4)}](\mathrm{ClO_4})_2$, $[\mathrm{La(AA)_2(NO_3)_2}](\mathrm{NO_3})$, $[\mathrm{La(AA)_2Cl_3}]$, $[\mathrm{La(AA)_2Br_2}]\mathrm{Br}$, and $[\mathrm{La(AA)_2I}]\mathrm{I_2}$. The Schiff base AA acts as a neutral terdentate ligand coordinating through both the carbonyl oxygens and through the azomethine nitrogen, giving two ring systems (one five-membered and the other six-membered). The TG and DTG curves of all five complexes are given in Figs. 1–5. The phenomenological aspects of the perchlorate, nitrate, chloride, bromide, and iodide complexes of lanthanum with the Schiff base AA are discussed here (Table 1).

The lanthanum perchlorate complex of AA $[\mathrm{La(AA)_2(ClO_4)}](\mathrm{ClO_4})_2$ is thermally stable up to about 200°C and undergoes decomposition in three stages (Table 1) as

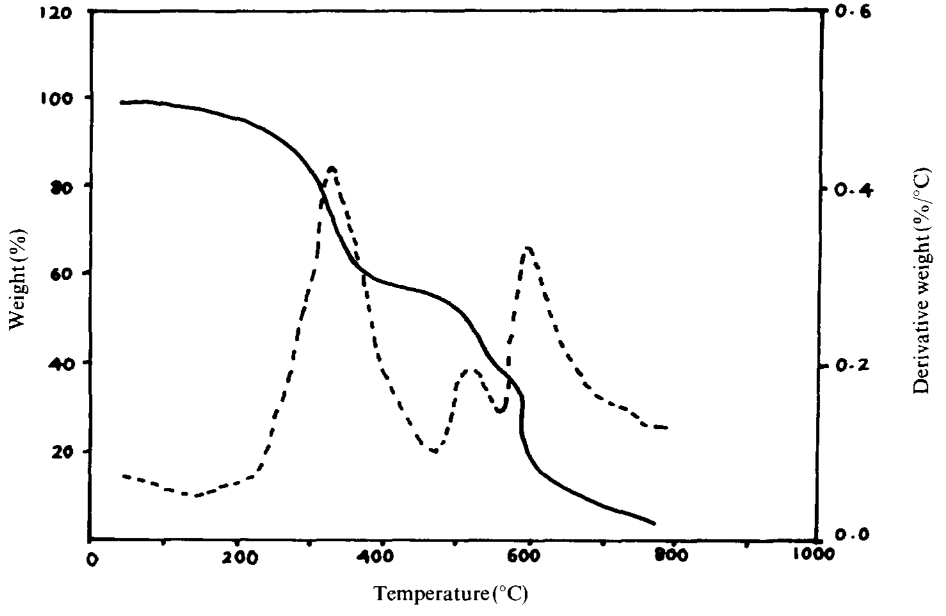

Fig. 1. TG and DTG curves of $[\mathrm{La(AA)_2ClO_4}](\mathrm{ClO_4})_2$ complex.

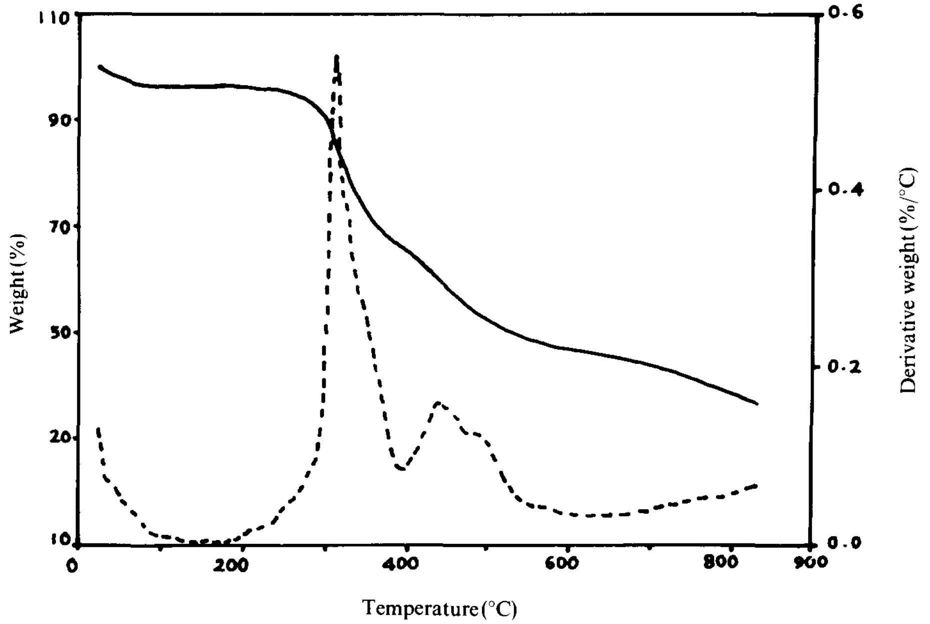

Fig. 2. TG and DTG curves of $[La(AA)_2(NO_3)_2](NO_3)$ complex.

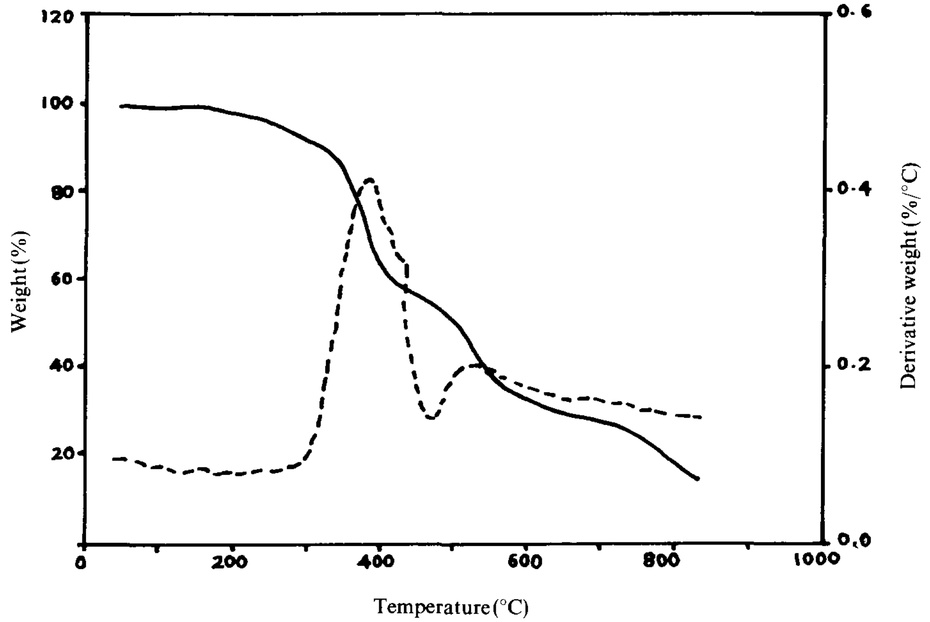

Fig. 3. TG and DTG curves of $[La(AA)_2Cl_3]$ complex.

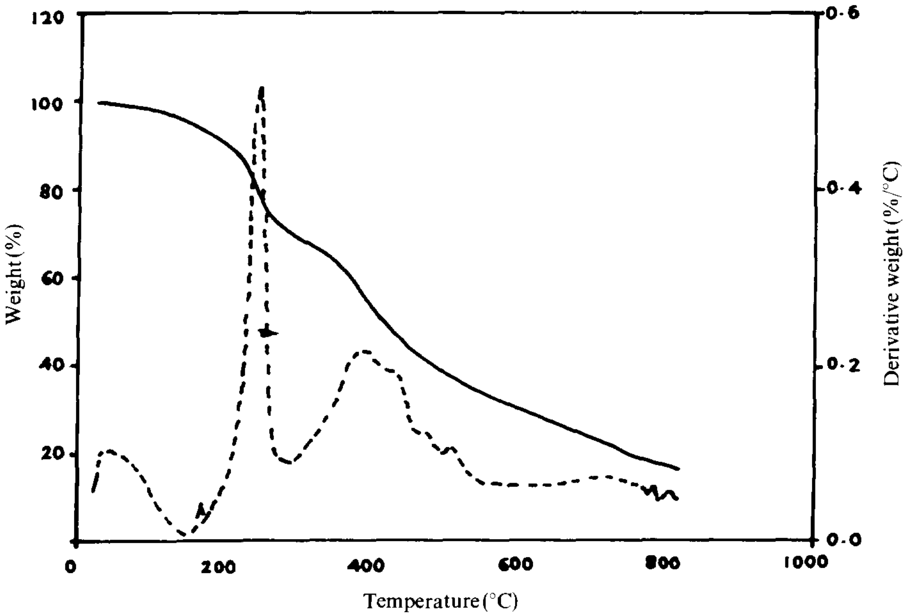

Fig. 4. TG and DTG curves of [La(AA)$_2$Br$_2$]Br complex.

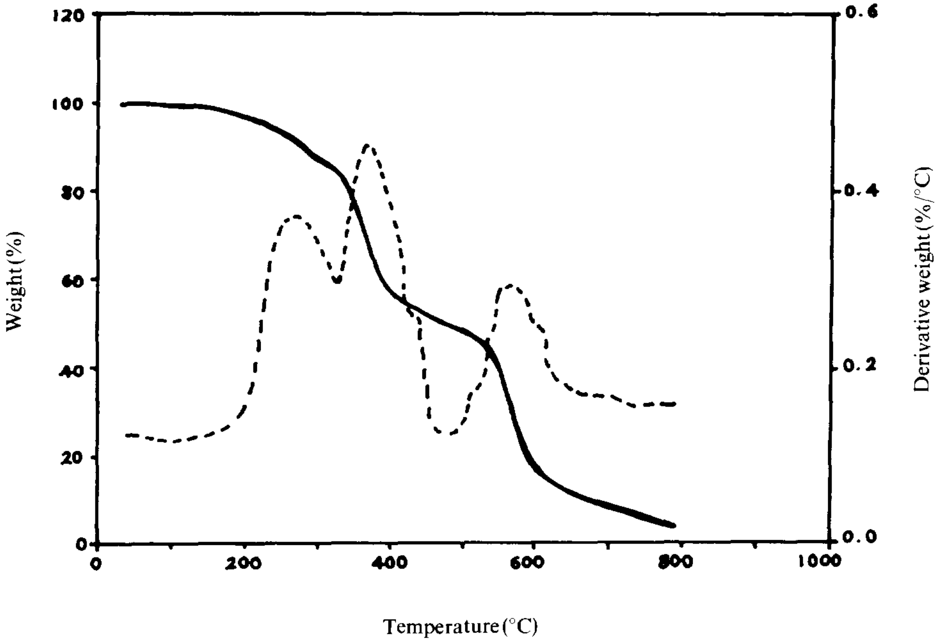

Fig. 5. TG and DTG curves of [La(AA)$_2$I]I$_2$ complex.

Table 1
Phenomenological data for the thermal decomposition of perchlorate, nitrate, chloride, bromide, and iodide complexes of lanthanum with AA

Complex	Stages of decomposition	TG Plateaux/°C	DTG peak/°C	% Mass loss found (calculated)
$[La(AA)_2(ClO_4)](ClO_4)_2$	I	220–410	325	41.23 (41.00)
	II	410–560	505	8.75 (8.66)
	III	560–620	590	38.35 (38.39)
$[La(AA)_2(NO_3)_2](NO_3)$	I	220–380	310	35.00 (35.52)
	II	380–700	440	40.00 (40.52)
$[La(AA)_2Cl_3]$	I	192–438	389	39.05 (38.88)
	II	438–756	510	38.90 (38.88)
$[La(AA)_2Br_2]Br$	I	180–290	248	33.50 (33.89)
	II	290–580	386	33.70 (33.89)
$[La(AA)_2I]I_2$	I	171–315	265	19.63
	II	315–470	356	30.26 (30.35)
	III	470–570	558	30.11 (30.35)

denoted by the DTG peaks at 325, 505 and 590°C. The first stage of decomposition corresponds to a mass loss of 41.23%, which may be attributed to the loss of one ligand molecule and the decomposition of the two perchlorate groups (outside the coordination sphere) to chlorate groups. The second stage with a mass loss of 8.75% may be due to the decomposition of the two chlorates into chlorides. The third and final decomposition stage amounts to a total loss of 38.95% which is assigned to the loss of the second ligand molecule and the conversion of the perchlorate group inside the coordination sphere into chloride, resulting in the formation of anhydrous lanthanum chloride. On further heating, the anhydrous lanthanum chloride undergoes sublimation [14] and a steady mass loss is observed. The final product formed was confirmed by qualitative analysis.

The lanthanum nitrate complex $[Ln(AA)_2(NO_3)_2](NO_3)$ undergoes decomposition in two stages giving the stable lanthanum oxide as the final residue. The first stage of decomposition starts at about 220°C corresponding to a mass loss of 35% which may be attributed to the loss of one ligand molecule. The second stage of decomposition occurs with a mass loss of 40% which may be due to loss of the second ligand molecule and the conversion of lanthanum nitrate into anhydrous lanthanum oxide. These two stages are denoted by the DTG peaks at about 310 and 440°C, respectively.

The lanthanum chloride complex $[La(AA)_2Cl_3]$ shows decomposition in two stages in the ranges 192–438 and 438–756°C as indicated by the DTG peaks at 389 and 510°C respectively. The complex is thermally stable up to 162°C and the first decomposition amounts to a mass loss of 39.05% which is attributed to the loss of one of the ligand species. The second stage of decomposition follows a mass loss of 38.90% which may be due to the loss of the second ligand molecule yielding the anhydrous lanthanum chloride which undergoes sublimation as denoted by a steady mass loss in TG. The final decomposition product is qualitatively tested and confirmed.

The lanthanum bromide complex $[La(AA)_2Br_2]Br$ shows two decomposition stages as denoted by the DTG peaks at 248 and 386°C. The first stage of decomposition corresponds to a mass loss of 33.50% which may be due to the loss of one ligand molecule. The second stage corresponds to a mass loss of 33.70% which may be attributed to the loss of the second ligand species yielding the anhydrous lanthanum bromide as the final product which is confirmed by qualitative analysis. The two stages of decomposition occur in the ranges 180–290 and 290–580°C. On further heating, the anhydrous lanthanum bromide undergoes sublimation and a steady mass loss is observed.

The lanthanum iodide complex $[La(AA)_2I]I_2$ undergoes decomposition in three stages as indicated by the DTG peaks obtained at 265, 356 and 558°C. The decomposition of the complexes corresponds to the mass losses of 19.63, 30.26 and 30.11% respectively. The first stage corresponds to the partial decomposition of the iodide group, while the second and third stages correspond to the loss of ligand molecules one by one. Finally, the mixed iodide of La(II) and La(III) is formed [15] which undergoes sublimation and a steady mass loss is observed.

From the thermal studies of the lanthanum perchlorate, nitrate, chloride, bromide, and iodide complexes of AA, it is concluded that the nature of the decomposition changes with the anion, even though all the complexes contain two ligand units. The perchlorate and iodide complexes show three-stage decompositions, and the others two-stage decompositions. Both the perchlorate and nitrate complexes of lanthanum contain two AA molecules and oxygen-coordinated anionic species inside the coordination sphere and, hence, their thermal stability is more or less the same. But the thermal stabilities of the halide complexes are less than those of the perchlorate and nitrate complexes, decreasing in the order: chloride > bromide > iodide. All these complexes contain two AA units and hence the stability is related to the nature of the anion. The size of the halide ions increases in the order chloride < bromide < iodide; therefore, the strain at the central atom increases in the same order, hence the decreasing order of thermal stability. The thermal stability of the lanthanum complexes follows the order: perchlorate ≈ nitrate > chloride > bromide > iodide.

3.1. Kinetic aspects

The kinetic evaluation of the thermal decomposition of the complexes was carried out using a computer program. Stages I and II were selected for the study of the kinetics of decomposition of the complexes. In almost all the complexes these stages include the decomposition of the ligand part. The kinetic parameters, the activation energy E and the pre-exponential factor A, were calculated using the Coats-Redfern equation [16]

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

A plot of the LHS of this equation against $1/T$ must give a straight line. Here, $\log[g(\alpha)/T^2]$ versus $10^3/T$ plots give a straight line whose slope and intercept are used for calculating the kinetic parameters by the least-squares method. The goodness of fit was tested by evaluating the correlation coefficient.

The entropy of activation ΔS can be calculated using the equation

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

where k is Boltzmann's constant, h Planck's constant, and S the entropy of activation.

Elucidation of the mechanism for the solid-state thermal decomposition reaction is difficult. All the heterogeneous processes can be classified into three categories: nucleation and growth; diffusion; and phase boundary reactions. Several kinetic equations have been derived corresponding to the above three possible rate-determining steps. The kinetic equations which govern the reaction mechanism are based on the assumption that the form of $g(\alpha)$ depends on the reaction mechanism. Here in the present investigation, nine forms of $g(\alpha)$, as denoted by Satava [17], have been used. The form of $g(\alpha)$ best representing the experimental data is considered as the mechanism of the reaction. We have calculated the kinetic parameters of the thermal decomposition of lanthanum perchlorate, nitrate, chloride, bromide, and iodide complexes of AA using both stages I and II of the decomposition in nitrogen atmosphere. The highest value of the correlation coefficient is for $g(\alpha) = -\ln(1-\alpha)$, which is the random nucleation mechanism with one nucleus on each particle. This represents the 'Mampel model'.

The kinetic parameters of the decomposition reactions of the complexes of lanthanum with Schiff base AA are given in Table 2. There is no regular variation in the values of the kinetic parameters of decomposition of the complexes as with other common physical constants, namely boiling point, melting point, etc. The activation energy of the decomposition reactions is in the range 42–226 kJ mol^{-1} which indicates that the metal–ligand bond is very weak [14, 18]. The values of E are comparable with the activation energy of dehydration of the hydrated salts. This indicates that the ligands are loosely bound to the metal ion through electrostatic forces, because 4f electrons shielded by the $5s^25p^6$ octet are not available for covalent bonding. There is no definite trend in the values of the energy of activation or the 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 and that the reactions are slower than normal [19, 20].

Table 2
Kinetic parameters of the thermal decomposition of lanthanum complexes AA

Complex	Stage	$E/(\text{kJ mol}^{-1})$	$A/(\text{s}^{-1})$	$\Delta S/(\text{J mol}^{-1})$
Lanthanum perchlorate	I	42.90	1.06×10^2	−269.16
	II	226.88	3.25×10^4	−166.54
Lanthanum nitrate	I	106.27	7.37×10^2	−214.78
	II	109.94	1.59×10^3	−229.14
Lanthanum chloride	I	85.58	3.47×10^2	−220.03
	II	110.39	6.75×10^2	−237.06
Lanthanum bromide	I	107.24	4.66×10^2	−198.51
	II	54.59	3.21×10^3	−264.35
Lanthanum iodide	I	86.79	5.87×10^3	−218.07
	II	178.99	3.72×10^2	−192.99

Acknowledgements

We thank Dr. P.M. Madhusudanan for helpful discussions, the Director of this School for providing necessary facilities and the Head, RSIC, IIT, Madras and Bombay, India for some instrumental analyses. We also thank the authorities of the University Grants Commission, New Delhi, India for the award of a Senior Research Fellowship to one of us (MKM).

References

[1] W.W. Wendlandt and G.D. Ascenzo, J. Therm. Anal., 1 (1969) 423.
[2] W.W. Wendlandt and G.D. Ascenzo, Anal. Chim. Acta, 50 (1970) 79.
[3] W.W. Wendlandt and F.C. Chang, Thermochim. Acta, 2 (1971) 293.
[4] J.O. Hill, C.G. Scency and R.J. Magee, Thermochim. Acta, 11 (1975) 301.
[5] J.O. Hill, C.G. Scency, J.F. Smith and R.J. Magee, J. Therm. Anal., 9 (1976) 415.
[6] C.K. Bhaskare, P.G. More and P.P. Hankare, Proceedings of the National Symposium on Thermal Analysis, 1981, BARC, India.
[7] M. Lehtinen, Acta Pharm. Fenn., 90 (1981) 187.
[8] K.N. Johri and B.S., Arora, Thermochim. Acta, 54 (1982) 237.
[9] L. Pardeshi and R.A. Bhobe, Acta Cient. Indica, 9 (1983) 18.
[10] M.K. Muraleedharan Nair and P.K. Radhakrishnan, Polyhedron, 12 (1993) 1227.
[11] M.K. Muraleedharan Nair and P.K. Radhakrishnan, Synth. React. Inorg. Met.-org. Chem., (1995) in press.
[12] M.K. Muraleedharan Nair and P.K. Radhakrishann, Proc. Indian Acad. Sci. (Chem. Sci.), 107 (1995) 19.
[13] M.K. Muraleedharan Nair, Ph.D. Thesis, Mahatma Gandhi University, Kottayam, 1994.

[14] T. Ganga Devi, K. Muraleedharan and M.P. Kannan, Thermochim. Acta, 191 (1991) 105.
[15] J.A. Dean (ed.), Lange's Hand Book of Chemistry, 13th edn., McGraw-Hill Book Company, New York, 1976.
[16] A.W. Coats and J.P. Redfern, Nature, 210 (1964) 68.
[17] V. Satava, Thermochim. Acta, 2 (1971) 423.
[18] M. Nath, Thermochim. Acta, 185 (1991) 11.
[19] S. Mathew, CGR Nair and K.N. Ninan, Thermochim. Acta, 144 (1989) 33.
[20] K.K. Aravindakshan and K. Muraleedharan, Thermochim. Acta, 155 (1989) 247.