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# THERMAL DECOMPOSITION KINETICS OF LANTHANUM COMPLEXES OF 1,2-(DIIMINO-4'-ANTIPYRINYL)ETHANE

*M. K. M. Nair and P. K. Radhakrishnan*[1]

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

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## Abstract

The kinetics and mechanism of the thermal decomposition of perchlorate, nitrate and iodide complexes of lanthanum with the Schiff base 1,2-(diimino-4'-antipyrinyl)ethane (abbreviated as GA) have been studied by TG and DTG techniques. The kinetic parameters like the activation energy, the pre-exponential factor and the entropy of activation were calculated for the major decomposition stages (Stages I and II) using Coats-Redfern equation. The rate controlling process obey 'Mampel model' with random nucleation with one nucleus on each particle. The kinetic parameters indicate that the ligands are loosely bound to metal ion and the activated complex formed in the decomposition reaction is more ordered than the reactants.

**Keywords:** complexes of lanthanum, entropy of activation, kinetics

## Introduction

Very few systems have been reported showing the relationship between the thermal stability of metal chelates and the structure of the chelating reagents [1]. Wendlandt and coworkers [2–4] and Hill and coworkers [5, 6] studied the thermal properties of metal chelates in the different types of complexing ligand. Such studies on thermal decomposition and kinetics of metal chelates with Schiff base ligands have been carried out by a few workers [7, 8]. In the present communication we report our studies on thermogravimetric analysis and kinetics of the thermal decomposition of the perchlorate, nitrate and iodide complexes of lanthanum with the Schiff base derived from antipyrine, viz., 1,2-(diimino-4'-antipyrinyl)ethane (Empirical formula: $C_{24}H_{24}N_6O_2$).

1 Author to whom all correspondence should be addressed.

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## Experimental

The Schiff base and the complexes of lanthanum were prepared as reported earlier [9–11]. Thermal analysis was carried out using Shimadzu DT-40 and DuPont 2000 thermal analysers in nitrogen atmosphere. A constant heating rate of 10°C $min^{-1}$ and a sample mass of about 10 mg were employed for the entire study. (No special precaution is needed for the thermal study of the present perchlorate complexes at the reported heating rate and sample amount in nitrogen atmosphere.)

### *Treatment of data*

The kinetic evaluation of the thermal decomposition of the above complexes were conducted using a computer programme. The Stage I and II were selected for the study, which include the step-wise decomposition of the ligand part. The kinetic parameters such as the activation energy ($E$) and the pre-exponential factor ($A$) were calculated using the Coats-Redfern equation [12].

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

A plot of LHS of the equation against $1/T$ must give a straight line. In our present work, $\log[g(\alpha)/T^2]$ *vs.* $10^3\ T^{-1}$ give straight line graph, whose slope and intercept are used for calculating the kinetic parameters by least square method. The goodness of fit was tested by calculating the correlation coefficient.

The entropy of activation ($\Delta S$) can be calculated using the equation

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

where $k$=Boltzman constant and $h$=Plank's constant.

## Results and discussion

The elemental analyses, electrical conductance in non-aqueous media, magnetic moments, infrared, electronic and proton NMR spectra show that the present complexes have the following formulae: $[La(GA)_2(ClO_4)](ClO_4)_2$, $[La(GA)_2(NO_3)_3]$ and $[La(GA)_2I]I_2$. GA acts as a neutral tetradentate ligand coordinating through both the carbonyl oxygens and both the azomethine nitrogens resulting three five-membered chelate rings and one of the perchlorates, all the three nitrates and one of the iodides are coordinated monodentately to the metal ion.

## *Phenomenological aspects*

The phenomenological aspects of the present complexes are presented in Table 1.

The lanthanum perchlorate complex $[La(GA)_2(ClO_4)](ClO_4)_2$ is thermally stable up to about 200°C and decompose in two stages (Table 1) as denoted by the DTG peaks at 320 and 600°C. The first stage of decomposition amounts to 48.2%, which may be assigned to the loss of one ligand and conversion of perchlorate to chloride group. The second stage of decomposition occurs with a mass loss of 32.9% which may be due to the decomposition of the second ligand part giving anhydrous lanthanum chloride as the final product. At high tempera-

**Table 1** Phenomenological data for the thermal decomposition of the perchlorate, nitrate and iodide complexes of lanthanum with GA

| Complexes | Stages of decomposition | TG plateaux/ °C | DTG peak/ °C | Mass loss/% found (calculated) |
|---|---|---|---|---|
| $[La(GA)_2(ClO_4)](ClO_4)_2$ | I | 220–375 | 320 | 48.20 (48.80) |
| | II | 375–625 | 600 | 32.90 (33.30) |
| $[La(GA)_2(NO_3)_3]$ | I | 220–430 | 380 | 40.00 (41.10) |
| | II | 430–550 | 470 | 36.10 (36.40) |
| $[La(GA)_2I]I_2$ | I | 170–440 | 350 | 32.00 (31.50) |
| | II | 440–750 | 620 | 31.00 (31.50) |

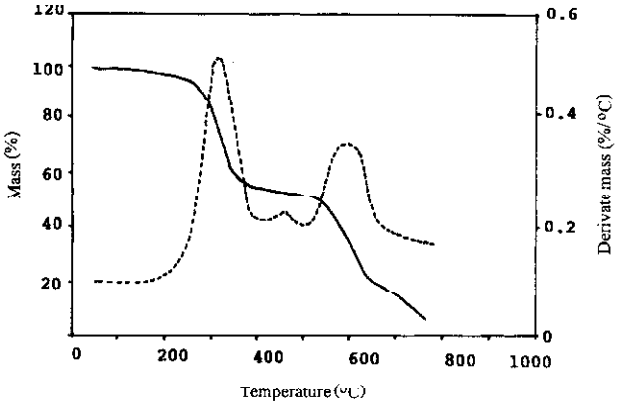


**Fig. 1** TG and DTG curves of $[La(GA)_2(ClO_4)](ClO_4)_2]$ complex

ture the anhydrous lanthanum chloride undergoes sublimation and a steady continuous mass loss was observed. The final product formed was confirmed by qualitative analysis.

The lanthanum nitrate complex $[La(GA)_2(NO_3)_3]$ is stable up to 200°C and undergoes decomposition in two stages as indicated by the DTG peaks at 380 and 470°C. The first stage corresponding to a mass loss of 40%, may be due to the loss of one ligand and the decomposition of nitrate group. The second stage amounting to a mass loss of 36.1% may be assigned to the loss of second ligand species along with complete conversion of the nitrate to the stable anhydrous lanthanum oxide.

The lanthanum iodide complex $[La(GA)_2I]I_2$ is stable up to 150°C and shows two-stage decomposition pattern (Table 1) as represented by the DTG peaks at 350 and 620°C. The first stage corresponds to a mass loss of 32% which may be assigned to the decomposition of one ligand molecule. The second stage of de-

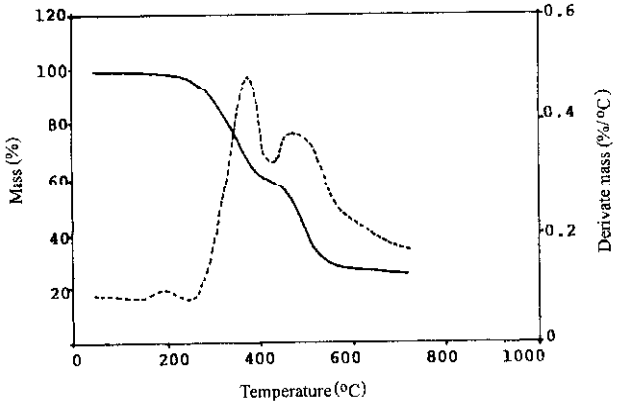


**Fig. 2** TG and DTG curves of $[La(GA)_2(NO_3)_3]$ complex

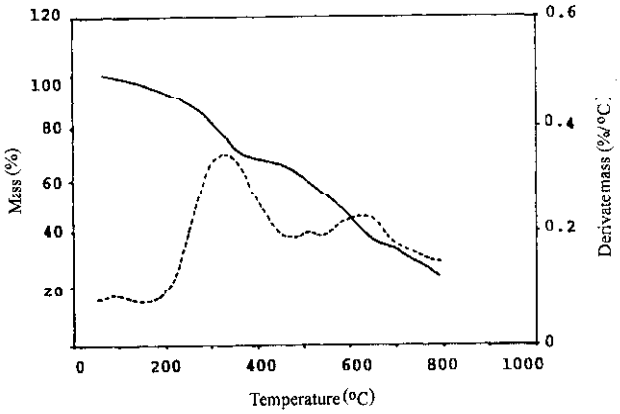


**Fig. 3** TG and DTG curves of $[La(GA)_2I]I_2$ complex

composition amounting to a mass loss of 31% may be assigned to the loss of the second ligand molecule yielding the anhydrous lanthanum iodide as the final product, which undergoes sublimation at high temperature as indicated by a steady continuous mass loss. The formation of anhydrous lanthanum iodide was confirmed by qualitative analysis.

From the thermal studies of the lanthanum perchlorate, nitrate and iodide complexes of GA, it is concluded that all the complexes are stable up to about 150–200°C. All the three types of complexes contain common metal ion and same number of ligands. The lanthanum perchlorate and nitrate complexes show similar thermal behaviour. But the lanthanide iodide complex is thermally less stable than the other two complexes. All the complexes undergo two-stage decomposition with step-wise loss of ligand molecules. But the decomposition temperatures vary with respect to the anion suggesting the variation in the strength of the metal-ligand bonds with change of anion. In perchlorate and nitrate complexes, due to the similarity in anionic size, similar thermal behaviour is observed. But in iodide complex, the steric strain due to the ligand molecule coupled with large iodide ion cause decreased stability, which is reflected in the TG data. Thus the thermal stability of various lanthanum complexes are in the order: perchlorate≈nitrate>iodide.

## *Kinetic aspects*

The kinetic parameters of the decomposition reaction of lanthanum complexes of GA are given in Table 2. The values of $E$ and $A$ for the lanthanum perchlorate and nitrate complexes are slightly higher in Stage II decomposition compared to the Stage I decomposition which indicate that Stage II is more ordered than Stage I. This may be expected due to the decreased steric strain when one ligand species is decomposed in the Stage I decomposition. The activation energy of decomposition reaction is in the range 43 to 116 kJ $mol^{-1}$ which indicates that the metal-ligand bond is very weak [14, 15]. The values of $E$ are comparable with the activation energy of dehydration of hydrated salts. This suggests

**Table 2** Kinetic parameters of the thermal decomposition of lanthanum complexes of GA

| Complexes | Stages of decomposition | $E$/ kJ $mol^{-1}$ | $A/s^{-1}$ | $\Delta S$/ J $mol^{-1}$ |
|---|---|---|---|---|
| Lanthanum perchlorate | I | 76.29 | $3.36 \cdot 10^2$ | −240.54 |
| | II | 102.33 | $3.02 \cdot 10^3$ | −251.46 |
| Lanthanum nitrate | I | 102.27 | $5.87 \cdot 10^2$ | −210.74 |
| | II | 115.29 | $3.31 \cdot 10^4$ | −228.22 |
| Lanthanum iodide | I | 43.58 | $1.01 \cdot 10^3$ | −270.62 |
| | II | 77.06 | $2.89 \cdot 10^2$ | −264.32 |

that the ligands are loosely bound to the metal ion. The negative value of the entropy of activation in all the complexes indicates that the activated complex has a more ordered structure than the reactants and the reactions are slower than normal [16, 17].

### *Mechanistic aspects*

The elucidation of mechanism for the solid state thermal decomposition reaction is a complicated one. The kinetic equation which govern the reaction mechanism is based on the assumption that the form of $g(\alpha)$ depends on the reaction mechanism. The nine forms of $g(\alpha)$ codified by Satava [13] have been used for investigation. The form of $g(\alpha)$ giving best experimental data is considered as the mechanism of the reaction. We have calculated the kinetic parameters of the thermal decomposition of lanthanum perchlorate, nitrate and iodide complexes of GA using both Stage I and Stage 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 with one nucleus on each particle, which represents the 'Mampel model'.

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