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Thermal decomposition kinetics and mechanism of lanthanide perchlorate complexes of 4-*N*-(4′-antipyrylmethylidene)aminoantipyrine

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Abstract

The thermal decomposition behaviour of lanthanide perchlorate complexes of the Schiff base, 4-*N*-(4′-antipyrylmethylidene)aminoantipyrine (AA), have 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. © 1997 Elsevier Science B.V.

Keywords: Thermal decomposition; Kinetics; Mechanism; Lanthanide perchlorate

1. 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. The present investigation is concerned with the thermal decomposition behaviour of the lanthanide perchlorate complexes of the Schiff base, derived from antipyrine, viz., 4-*N*-(4′-antipyrylmethylidene)-aminoantipyrine (AA) (empirical formula: $C_{23}H_{23}N_5O_2$).

2. Experimental

The Schiff base and the complexes of lanthanide perchlorates were prepared as reported earlier [8,9]. Thermogravimetric analyses were carried out on Shimadzu-DT-40 and DuPont 2000 thermal analysers in an atmosphere of nitrogen (sample mass – 10 mg; heating rate – 20 K min^{-1}).

3. Results and discussion

All complexes were characterised by elemental analyses, magnetic susceptibility, infrared, proton NMR and electronic spectral studies. These complexes had the following general formulae: $[Ln(AA)_2(ClO_4)](ClO_4)_2$, where Ln=La, Pr, Nd,

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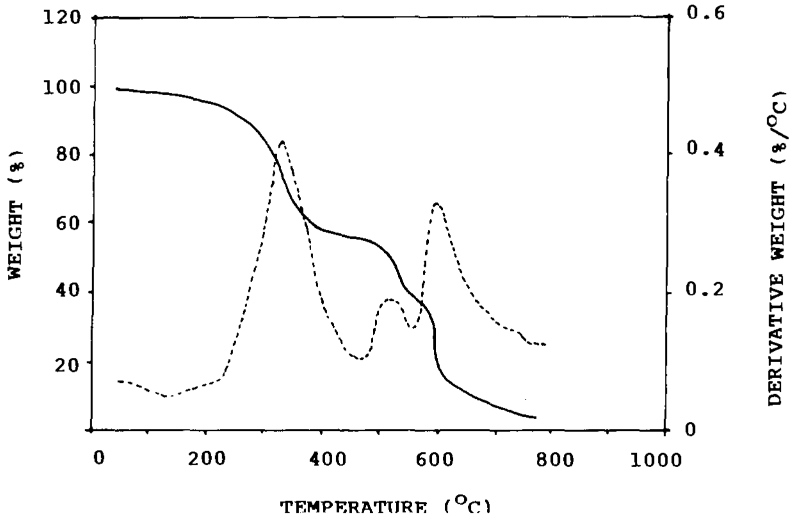

Fig. 1. TG and DTG curves of $[La(AA)_2(ClO_4)](ClO_4)_2$ complex.

Sm and Eu, and $[Ln(AA)_3](ClO_4)_3$, where Ln=Gd, Dy, Ho and Er. The Schiff base AA acts as a neutral tridentate ligand, coordinating both by carbonyl oxygens and the azomethine nitrogen, giving two-ring systems (one five-membered and the other six-membered). These two types of complexes show two patterns of decomposition (Figs. 1–9). The decomposition of the first type of complex is represented by the typical lanthanum complexes (Fig. 1) which exhibit three stages of decomposition (Table 1). The second type of complexes also show a three-stage decomposition as given in Table 1 represented by the gadolinium complex (Fig. 6).

3.1. Phenomenological aspect

The lanthanum perchlorate complex of AA $[La(AA)_2(ClO_4)](ClO_4)_2$ is thermally stable up to

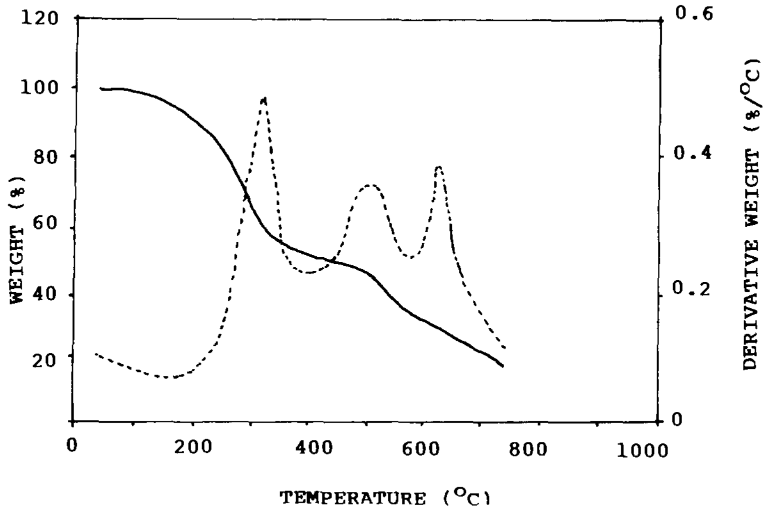

Fig. 2. TG and DTG curves of $[Pr(AA)_2(ClO_4)](ClO_4)_2$ complex.

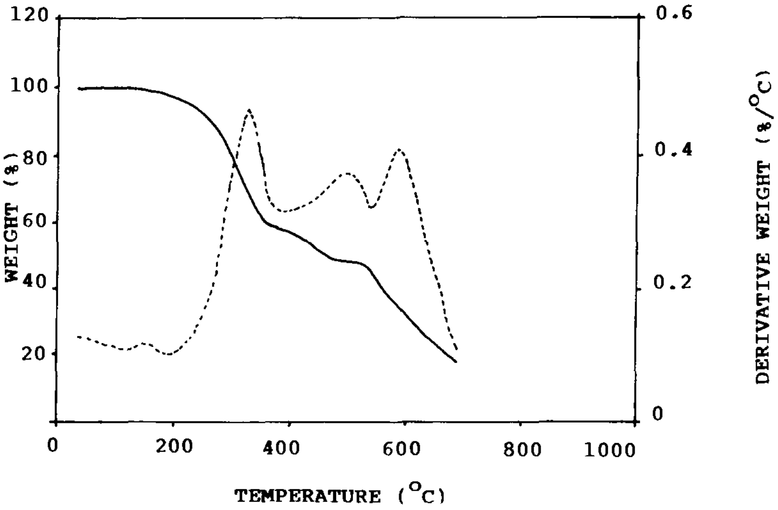

Fig. 3. TG and DTG curves of $[Nd(AA)_2(ClO_4)](ClO_4)_2$ complex.

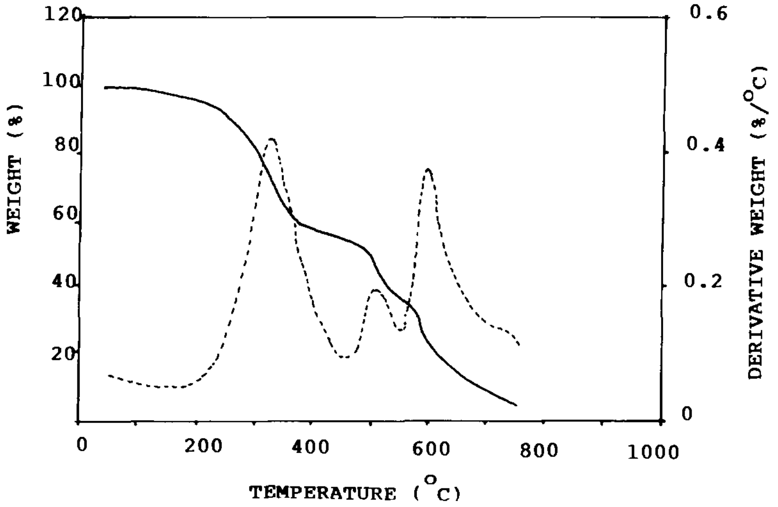

Fig. 4. TG and DTG curves of $[Sm(AA)_2(ClO_4)](ClO_4)_2$ complex.

~200°C and undergo decomposition in three stages (Table 1), as denoted by the DTG peaks at 325°, 505° and 590°C. The first stage of the decomposition corresponds to a mass loss of 41.23%, which can be attributed to the loss of one ligand molecule and the decomposition of the two perchlorate groups (outside coordination sphere) to chlorate group. The second stage with a mass loss of 8.75% may result from decomposition of the two chlorates into the chlorides. The third and final decomposition stage amounts to a total mass 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 and a steady mass loss is observed. The final product formed was confirmed by qualitative analysis. The same type

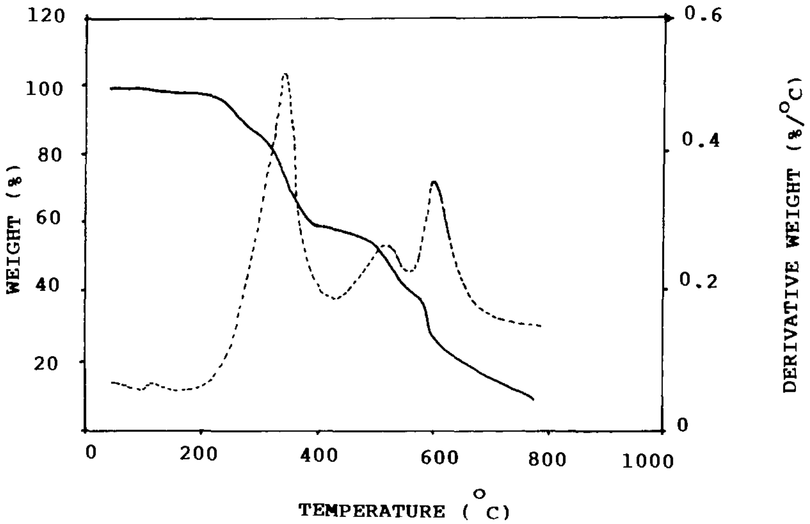

Fig. 5. TG and DTG curves of $[Eu(AA)_2(ClO_4)](ClO_4)_2$ complex.

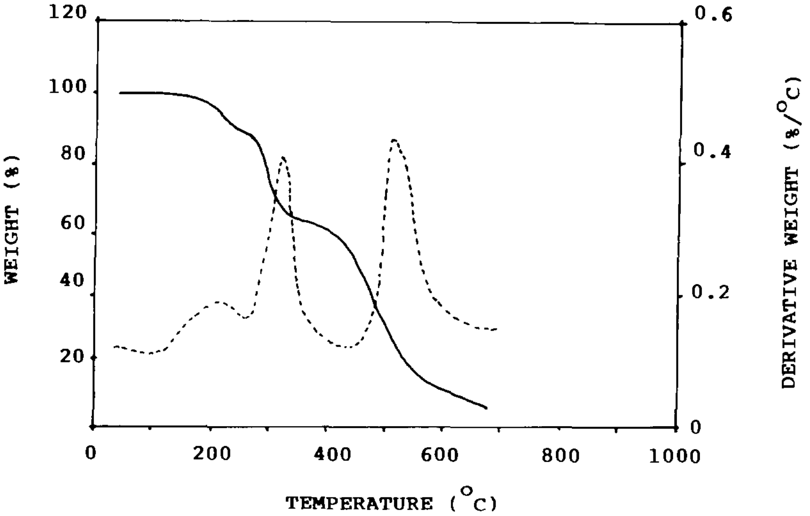

Fig. 6. TG and DTG curves of $[Gd(AA)_3](ClO_4)_3$ complex.

of decomposition pattern is observed in the case of Pr, Nd, Sm and Eu complexes also, which suggest the similar structure for these five complexes.

The gadolinium perchlorate complex of AA $[Gd(AA)_3](ClO_4)_3$ also shows three stages of decomposition as is evident from the DTG peaks at 210°, 312° and 508°C, and is thermally stable up to ~160°C. The first stage of decomposition with a mass loss of 8.6% may be attributed to the partial conversion of the perchlorate group into the chlorate group. The second stage, amounting to a mass loss of 30%, may be due to the loss of one ligand molecule along with complete conversion of chlorate group into chloride group. The third decomposition stage (48%) may be assigned to the loss of the remaining two ligand molecules, resulting in the final residue of anhydrous gadolinium chloride, a fact that was confirmed by the qualitative analysis. At high temperatures, the anhydrous gado-

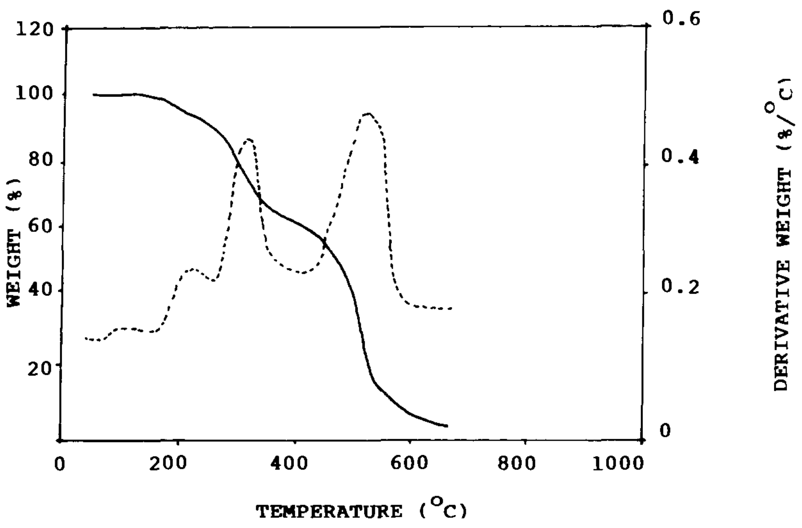

Fig. 7. TG and DTG curves of $[Dy(AA)_3](ClO_4)_3$ complex.

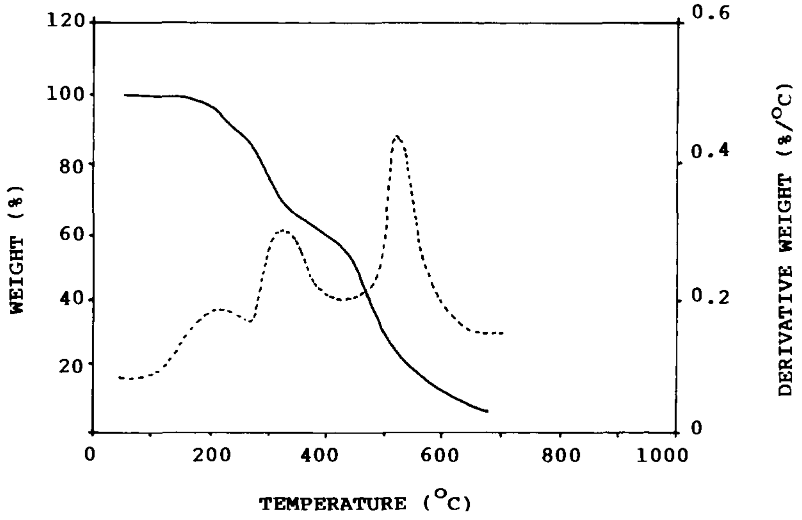

Fig. 8. TG and DTG curves of $[Ho(AA)_3](ClO_4)_3$ complex.

linium chloride undergoes sublimation and a steady mass loss is observed. Here also, the complexes of Dy, Ho and Er show the same decomposition pattern, which suggests the same structure for all these four complexes.

The perchlorate complexes of the light lanthanides, viz., La, Pr, Nd, Sm or Eu with AA, are thermally more stable than the corresponding perchlorate complexes of heavy lanthanides, viz., Gd, Dy, Ho and Er, which may be attributed to steric strain. The light lanthanide complexes contain two, and the heavy lanthanide complexes three ligand molecules. Thus, the steric strain in heavy lanthanide complexes makes it less thermally stable as is evident from TG.

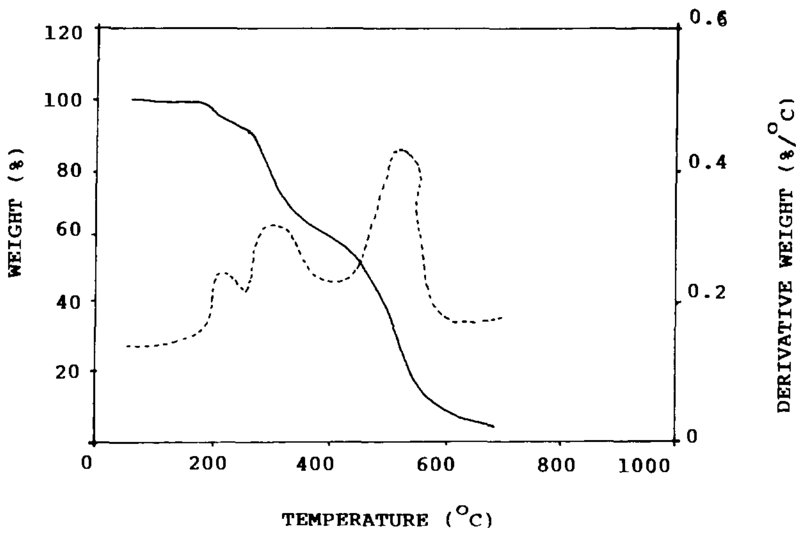

Fig. 9. TG and DTG curves of $[Er(AA)_3](ClO_4)_3$ complex.

Table 1
Phenomenological data for the thermal decomposition of lanthanide perchlorate complexes of AA.

Complexes	Stages of decomposition	TG plataeux (°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 (8.60)
	III	560–620	590	38.35 (38.39)
$[Pr(AA)_2(ClO_4)](ClO_4)_2$	I	220–420	320	41.40 (41.00)
	II	420–550	500	8.30 (8.56)
	III	550–650	610	38.50 (38.20)
$[Nd(AA)_2(ClO_4)](ClO_4)_2$	I	220–400	325	41.20 (41.00)
	II	400–560	510	8.40 (8.47)
	III	560–620	590	38.45 (38.15)
$[Sm(AA)_2(ClO_4)](ClO_4)_2$	I	220–400	320	41.50 (40.97)
	II	400–560	510	8.50 (8.40)
	III	560–630	600	38.50 (38.15)
$[Eu(AA)_2(ClO_4)](ClO_4)_2$	I	220–410	325	41.25 (40.90)
	II	410–560	500	8.55 (8.35)
	III	560–620	605	38.33 (38.05)
$[Gd(AA)_3](ClO_4)_3$	I	180–252	210	8.60 (8.50)
	II	252-336	312	30.00 (30.50)
	III	336–690	508	48.00 (48.80)
$[Dy(AA)_3](ClO_4)_3$	I	180–250	205	8.60 (8.50)
	II	250–340	320	30.00 (30.45)
	III	340–700	520	48.00 (48.20)
$[Ho(AA)_3](ClO_4)_3$	I	180–260	200	8.60 (8.45)
	II	260–345	325	30.00 (30.40)
	III	345–690	525	48.00 (48.17)
$[Er(AA)_3](ClO_4)_3$	I	180–255	205	8.70 (8.30)
	II	255–335	320	30.50 (30.35)
	III	335–700	520	48.50 (48.10)

Table 2
Kinetic parameters of the thermal decomposition of lanthanide perchlorate complexes of AA.

Complexes	Stages of decomposition	E/(kJ/mol)	A/(s^{-1})	ΔS/(J/mol)
$[La(AA)_2(ClO_4)](ClO_4)_2$	I	42.90	1.06×10^2	−269.16
	III	226.88	3.25×10^4	−166.54
$[Pr(AA)_2(ClO_4)](ClO_4)_2$	I	134.55	6.41×10^7	−203.48
	III	32.65	3.45×10^2	−278.08
$[Nd(AA)_2(ClO_4)](ClO_4)_2$	I	44.26	1.25×10^2	−267.15
	III	185.41	1.97×10^3	−189.70
$[Sm(AA)_2(ClO_4)](ClO_4)_2$	I	184.40	1.62×10^3	−191.45
	III	46.35	1.93×10^2	−264.21
$[Eu(AA)_2(ClO_4)](ClO_4)_2$	I	119.26	2.08×10^2	−227.36
	III	50.57	3.34×10^2	−255.36
$[Gd(AA)_3](ClO_4)_3$	II	161.88	4.25×10^2	−202.58
	III	80.50	8.21×10^4	−244.28
$[Dy(AA)_3](ClO_4)_3$	II	55.83	4.31×10^3	−295.86
	III	180.49	4.59×10^2	−202.95
$[Ho(AA)_3](ClO_4)_3$	II	98.09	6.62×10^2	−215.23
	III	236.78	7.21×10^4	−159.91
$[Er(AA)_3](ClO_4)_3$	II	74.56	3.21×10^3	−231.27
	III	148.72	4.20×10^2	−212.59

3.2. *Kinetic aspect*

The kinetic parameters of the thermal decomposition of complexes were evaluated using a computer programme. Stages I and III of La, Pr, Nd, Sm and Eu complexes and stages II and III of Gd, Dy, Ho and Er complexes 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 Coats–Redfern equation [10] was used for calculating the kinetic parameters, such as the activation energy (E) and the pre-exponential factor (A). The equation is:

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

A straight line graph will be obtained if we plot LHS of this equation vs. $1/T$. In our present work, $\log[g(\alpha)/T^2]$ vs. $1000/T$ gave a straight line graph, whose slope and intercept are used for calculating the kinetic parameters by the least squares method. The goodness of fit was tested by evaluating the correlation coefficient.

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

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

where, k is the Boltzmann constant and h the Planck constant.

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, the nine forms of $g(\alpha)$ codified by Satava [11] have been used. The form of $g(\alpha)$ representing the best experimental data is considered as the mechanism of the reaction. The highest value of correlation coefficient was for $g(\alpha) = -\ln(1 - \alpha)$ 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, lanthanide perchlorates with Schiff base AA 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 like other common physical constants, namely boiling point, melting point, etc. The activation energy of the decomposition stages varies in the range 32–237 kJ/mol. This value is very low and is comparable with the activation energy of the dehydration of hydrated salts [12,13]. 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. There is no proper variation for the values of E in the present series. Also, entropy of activation follows no definite trend. However, the ΔS values are negative for all the complexes in both stages of decomposition. The negative values indicate that the activated complex has a more ordered structure than the reactants and that the reactions are slower than normal [14,15].

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