

Kinetics and mechanism of the thermal decomposition of Schiff base complexes of lanthanides by TG and DSC studies

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Abstract

The thermal decomposition of lanthanum(III) and cerium(IV) chelates of acetylacetonaminofluorene was studied by TG and DSC. The mechanism of the decomposition has been established from TG and DSC data. The kinetic parameters, namely activation energy E , pre-exponential factor A and entropy of activation ΔS , were calculated from the TG and DSC curves using mechanistic and non-mechanistic integral equations.

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 co-workers [2–5] and Hill and co-workers [6,7] studied the thermal properties of metal chelates with different types of complexing ligands. Such studies on thermal decomposition and kinetics of metal chelates with azomethine ligands have been carried out by a few workers [8–11]. In continuation of our work [12–14] on thermal decomposition kinetics of metal chelates, we report in this paper the preparation, characterisation and thermoanalytical data for two lanthanide complexes of a novel Schiff base, acetylacetonaminofluorene.

Non-isothermal methods have been widely used to study the kinetics and mechanism of thermal decomposition of solids [15–17]. This study therefore attempts to establish the mechanism of decomposition of $[\text{CeL}_2(\text{OH})_2]$ and $[\text{LaLCl}_2(\text{H}_2\text{O})_2]$ from TG, DTG and DSC experiments.

EXPERIMENTAL

The ligand was prepared from 2-aminofluorene and acetylacetonone following the procedure reported by Schiff. Samples of cerium(IV) and lanthanum(III) chelates of acetylacetonaminofluorene were prepared by adding an ethanolic solution of the ligand to the metal chloride or sulphate

solution in a 2:1 ratio. The mixture was refluxed for 3 h and aqueous ammonia (1:20) was then added dropwise until turbidity appeared.

The precipitates were filtered off, washed with an ethanolic solution of the reagent and dried in a vacuum desiccator. The purity of the samples was checked by elemental analysis for the metal and C, H, N analysis. The structures of the two chelates were found to be $[\text{CeL}_2(\text{OH})_2]$ and $[\text{LaLCl}_2(\text{H}_2\text{O})_2]$.

INSTRUMENTAL

The IR spectra were recorded using a Perkin-Elmer Model 283 infrared spectrophotometer. Thermal analysis was carried out using a Perkin-Elmer 7 series thermal analysis system. A constant heating rate of $10^\circ\text{C min}^{-1}$ and a sample mass of ≈ 5 mg were employed for the entire study. The atmosphere was static air. The fractional decomposition α , was determined directly from the TG curves, whereas for the DSC experiment α was determined from the ratio of the fractional and total areas under the curve. Computational work was performed with a Horizon III mini-computer using the programming language Fortran.

The complexes were characterised on the basis of elemental analysis, and spectral and thermal studies. The infrared spectra of the chelates indicate the absence of characteristic absorption for the $-\text{OH}$ group and a shift in $\nu\text{C}=\text{N}$, showing that $-\text{OH}$ and $\text{C}=\text{N}$ are involved in coordination. Characteristic bands of H_2O are present in spectra of the lanthanum chelate. On steric grounds, one can assign octahedral structures for the complexes.

MATHEMATICAL ANALYSIS OF DATA

The TG curve for $[\text{CeL}_2(\text{OH})_2]$ exhibited a single stage decomposition pattern and that for $[\text{LaLCl}_2(\text{H}_2\text{O})_2]$ exhibited a three-stage decomposition pattern. The last stage represents the major decomposition step in the second case, and mass loss considerations and X-ray diffraction data confirmed the products to be the corresponding oxides. The thermograms are represented in Figs. 1 and 2.

Evaluation of the mechanism of reactions from non-isothermal methods has been discussed by Šesták and Berggren [18] and Satava [19]. The procedure is based on the assumption that the non-isothermal reaction proceeds isothermally in an infinitesimal time interval, so that the rate can be expressed by an Arrhenius-type equation

$$\frac{d\alpha}{dt} = A e^{-E/RT} f(\alpha) \quad (1)$$

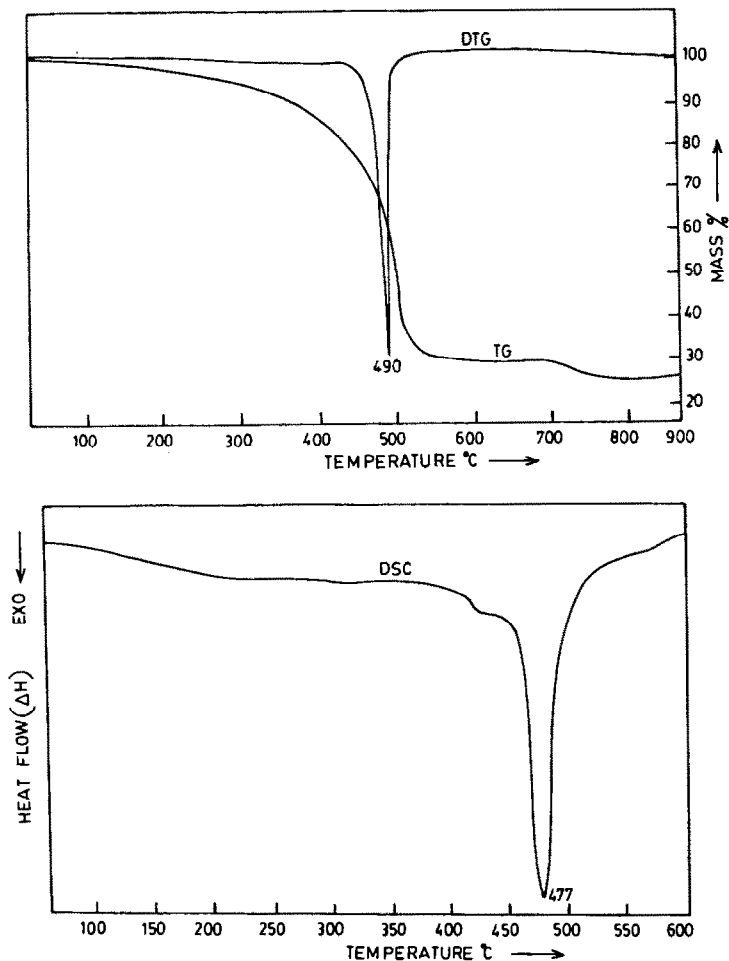


Fig. 1. TG, DTG and DSC of $\text{CeL}_2(\text{OH})_2$.

where A is the pre-exponential factor, t is the time and $f(\alpha)$ depends on the mechanism of the process. For a linear heating rate, ϕ , $dT/dt = \phi$ and substitution into eqn. (1) gives

$$\frac{d\alpha}{f(\alpha)} = \int_0^T \frac{A}{\phi} e^{-E/RT} dT \quad (2)$$

Integration of the left-hand side of eqn. (2) gives

$$\int_0^\alpha \frac{d\alpha}{f(\alpha)} = g(\alpha) = \int_0^T \frac{A}{\phi} e^{-E/RT} dT \quad (3)$$

where $g(\alpha)$ is the integrated form of $f(\alpha)$. A series of $f(\alpha)$ forms is proposed, and the mechanism is obtained from that which gives the best representation of the experimental data. Nine probable reaction mechanisms

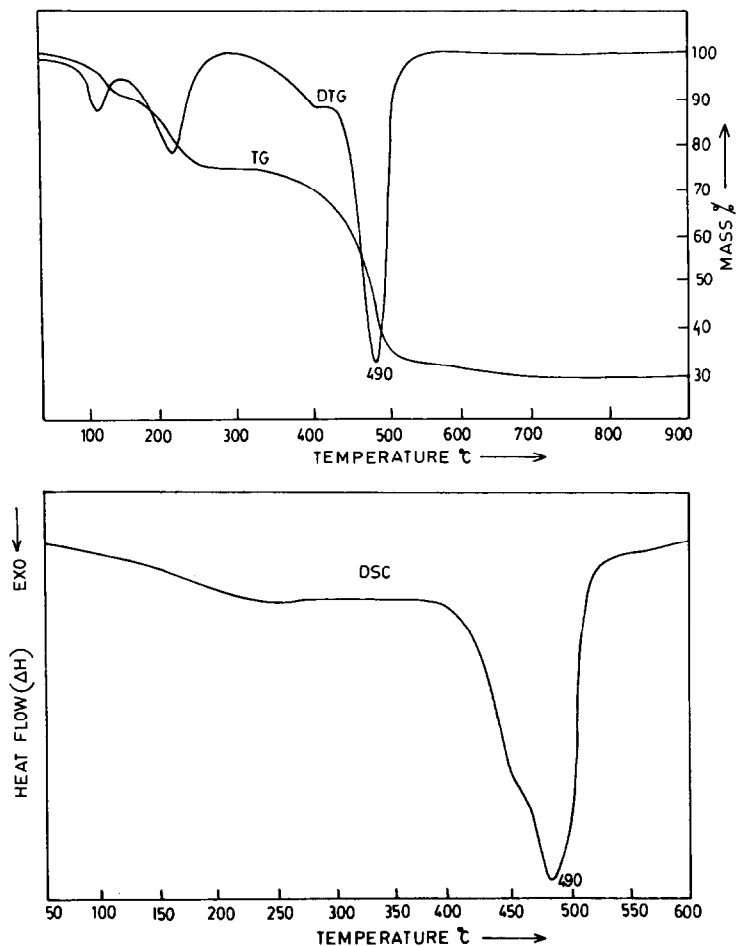


Fig. 2. TG, DTG and DSC of $\text{LaAlCl}_2(\text{H}_2\text{O})_2$.

given by Satava are shown in Table 1. For evaluating kinetic parameters from the mechanistic equations, the right-hand side of eqn. (3), the temperature integral which is an incomplete gamma function, was used in the form given by Coats and Redfern [20], which produces one of the best solutions and is recommended by several authors [21,22].

The general form of the equation used is

$$\ln \frac{g(\alpha)}{T^2} = \ln \frac{AR}{\phi E} - \frac{E}{RT} \quad (4)$$

Along with the mechanistic equations, two non-mechanistic methods suggested by Coats and Redfern [20] and by Horowitz and Metzger [23] were also used for comparison. The reaction order can easily be estimated by comparing the r values using $n = 0.33, 0.5, 0.66$ and 1 in the equations $1 - (1 - \alpha)^{1-n} / (1 - n) T^2$ vs. $1/T$ for $n \neq 1$

$$(5)$$

TABLE 1

Kinetic equations

Function	Equation	Rate-controlling process
D ₁	$\alpha^2 = Kt$	One-dimensional diffusion
D ₂	$(1 - \alpha) \ln(1 - \alpha) + \alpha = Kt$	Two-dimensional diffusion, cylindrical symmetry
D ₃	$[1 - (1 - \alpha)^{1/3}]^2 = Kt$	Three-dimensional diffusion, spherical symmetry; Jander equation
D ₄	$(1 - 2/3\alpha) - (1 - \alpha)^{2/3} = Kt$	Three-dimensional diffusion, spherical symmetry; Ginstling-Brounshtein equation
F ₁	$-\ln(1 - \alpha) = Kt$	Random nucleation, one nucleus on each particle; Mampel equation
A ₂	$-\ln(1 - \alpha)^{1/2} = Kt$	Random nucleation; Avrami equation I
A ₃	$-\ln(1 - \alpha)^{1/3} = Kt$	Random nucleation; Avrami equation II
R ₂	$1 - (1 - \alpha)^{1/2} = Kt$	Phase boundary reaction, cylindrical symmetry
R ₃	$1 - (1 - \alpha)^{1/3} = Kt$	Phase boundary reaction, spherical symmetry

$$\log[-\log(1 - \alpha)]/T^2 \text{ vs. } 1/T \text{ for } n = 1 \quad (6)$$

Kinetic parameters are calculated for the Ce(IV) complex from the DSC curve using the method proposed by Rogers and co-workers [24,25]. The distances between the baseline and the exothermic curve at different temperatures are measured. The distance is proportional to the rate of heat evolution at the particular temperature, and this rate is in turn proportional to the rate constant. A number of data points were taken between the onset and the maximum of the curve. Plots of logarithm of distance vs. reciprocal absolute temperature ($1/T$) were made, and from the plot the best linear portion of the curve was chosen. The distances d_1 and d_2 are the two extremes at the linear portion of the curves and the corresponding temperatures are T_1 and T_2 . By substituting the values of d_1 , d_2 , T_1 and T_2 in the equation

$$-E = \frac{4.58 \log(d_1/d_2)}{1/T_1 - 1/T_2} \quad (7)$$

the energy of activation, E , was calculated. The pre-exponential factor A was calculated by substituting the value of E in the equation

$$A = \frac{\phi E e^{E/RT_{\max}}}{RT_{\max}^2} \quad (8)$$

where ϕ is the linear heating rate, R is the gas constant and T_{\max} is the maximum of the DSC curves.

RESULTS AND DISCUSSION

The decomposition temperature ranges for the metal chelates are given in Table 2. Data from independent pyrolytic experiments are also included in

TABLE 2

Thermal decomposition data

Substance	Peak temp. in DTG (°C)	Peak temp. in DSC (°C)	Temp. ranges in DTG (°C)	Loss of mass (%)			Probable assignment
				From TG	Theoretical	From pyrolysis	
[CeL ₂ (OH) ₂]	490	477	150–600	75	75.35	75	loss of 2L
[LaLCl ₂ (H ₂ O) ₂]	1 120	–	90–175	7	7.08	–	loss of 2H ₂ O
	2 230	–	175–250	14	13.9	–	loss of Cl ₂
	3 490	490	250–510	45	46.85	67.9	loss of L
Total mass loss				66	67.83	67.9	

this table. The kinetic parameters calculated from TG and DSC (for stage III of the La complex) for the nine mechanistic equations are given in Table 3. The corresponding values of E , A , ΔS and r from non-mechanistic equations (Coats–Redfern, Horowitz–Metzger and Rogers) for the Ce(IV) complex are given in Table 4.

The DTG and DSC curves for [CeL₂(OH)₂] show a single peak. The very strong peak at 490 °C is a well-defined and non-overlapping one. Mass loss at the end of this stage, read from the TG curve, is 75%. An X-ray diffraction study showed that the final product is CeO₂. The theoretical mass loss at this stage for the decomposition of [CeL₂(OH)₂] to CeO₂ would be 75.35% if we assume that the other decomposition products have been completely volatilized.

In the case of [LaLCl₂(H₂O)₂], a three-stage decomposition pattern is observed. The main decomposition stage is represented by DTG and DSC peaks at 490 °C. The overall loss of mass from the TG curve is 66%, while the theoretical loss in mass for the conversion of [LaLCl₂(H₂O)₂] to La₂O₃ is 67.83%.

In the La(III) complex, two H₂O molecules are lost above 150 °C. According to Nikolaev et al. [26], water eliminated above 150 °C can be considered as coordinated water. Initial decomposition temperature and inflection temperature have been used to determine the thermal stability of metal chelates. In the present course of studies, based on observations made by earlier workers [27,28], the relative thermal stabilities of the lanthanide chelates can be given as [CeL₂(OH)₂] > [LaLCl₂(H₂O)₂].

DECOMPOSITION KINETICS

From Tables 3 and 4 it can be seen that more than one equation gives a good linear curve with a high value of correlation coefficient, so that it may

TABLE 3

Kinetic parameters for the decomposition of $[\text{Ce}_2(\text{OH})_2]$ and $[\text{LaCl}_2(\text{H}_2\text{O}_2)]$ from TG and DSC using mechanistic equations

Substance	Parameter ^a Mechanistic equation									
	1	2	3	4	5	6	7	8	9	
$[\text{Ce}_2(\text{OH})_2]$ TGA	<i>E</i>	36.9	43.3	51.2	45.9	28.4	12.7	7.5	22.1	24.1
	<i>A</i>	1.03×10^7	5.44×10^9	4.01×10^{11}	8.70×10^9	7.16×10^5	1.25×10^6	2.39×10^6	3.31×19^3	9.39×10^3
	ΔS	-31.16	-11.59	-7.31	-12.52	-30.44	-31.55	-23.69	-38.07	-35.56
$[\text{LaCl}_2(\text{H}_2\text{O}_2)]$ II Stage TGA	<i>r</i>	0.9979	0.9993	0.9996	0.9995	0.9987	0.9984	0.9981	0.9996	0.9996
	<i>E</i>	8.1	10.3	13.6	11.3	7.8	2.9	1.3	5.1	5.9
	<i>A</i>	6.72	6×10^1	9.22×10^2	4.57×10^1	1.38×10^1	0.028	0.002	0.177	0.347
III Stage TGA	ΔS	-59.48	-51.44	-46.01	-51.98	-59.60	-66.65	-71.67	-63.01	-61.68
	<i>r</i>	0.9967	0.9948	0.9854	0.9909	0.9652	0.9450	0.8983	0.9883	0.9813
	<i>E</i>	43.0	43.9	50.7	46.05	27.7	12.4	7.3	22.2	24.5
$[\text{LaCl}_2(\text{H}_2\text{O}_2)]$ III Stage DSC	<i>A</i>	1.09×10^{10}	1.15×10^{10}	4.29×10^{11}	1.26×10^{10}	5.82×10^5	8.41	0.15	4.21×10^3	1.37×10^4
	ΔS	-14.46	-14.36	0.1237	-14.18	-34.02	-56.17	-64.07	-43.82	-41.47
	<i>r</i>	0.9827	0.9950	0.9950	0.9926	0.9700	0.9636	0.9548	0.9896	0.9859
III Stage DSC	<i>E</i>	67.0	77.7	86.5	79.2	47.6	22.3	47.38	39.2	41.7
	<i>A</i>	1.06×10^{17}	1.01×10^{20}	1.26×10^{22}	7.05×10^{19}	4.65×10^{11}	9.59×10^3	1.26×10^{11}	5.24×10^8	2.26×10^9
	ΔS	17.50	31.14	36.26	30.41	-7.01	-42.18	-9.61	-20.50	-17.59
<i>r</i>	0.9981	0.9978	0.9995	0.9992	0.9996	0.9992	0.9996	0.9993	0.9995	

^a *E* in kcal mol⁻¹, *A* in s⁻¹, ΔS in kcal.

TABLE 4
Kinetic parameters for the decomposition of $[\text{CeL}_2(\text{OH})_2]$ and $[\text{LaLCl}_2(\text{H}_2\text{O})_2]$ from TG and DSC using non-mechanistic equations^a

Substance	Coats-Redfern			Horowitz-Metzger			Rogers			Order of reaction (n)	
	E	A	r	E	A	ΔS	r	E	A		ΔS
$[\text{CeL}_2(\text{OH})_2]$											
TG data	22.1	6.6×10^3	0.9996	26.8	1.9×10^5	-27.8	0.9953	36.6	1.5×10^8	-95.8	1/2
DSC data	-	-	-	-	-	-	-	-	-	-	-
$[\text{LaLCl}_2(\text{H}_2\text{O})_2]$											
TG data II stage	4.3	0.12	0.9921	7.1	1.07	-59.4	0.9983	-	-	-	1/3
$[\text{LaLCl}_2(\text{H}_2\text{O})_2]$											
TG data III stage	20.8	2.7×10^3	0.9944	26.5	1.4×10^5	-36.7	0.9974	-	-	-	1/3
DSC data III stage	36.6	1.6×10^9	0.9990	41.6	5.0×10^9	-16.0	0.9996	-	-	-	1/3

^a E in kcal mol⁻¹, A in s⁻¹, ΔS in kcal.

become difficult to assign the reaction mechanisms unequivocally from the linearity of the curve alone. In such cases, some authors have chosen the function $g(\alpha)$ which gives kinetic parameters in agreement with those obtained by the numerical method. In the present case, it is observed that for all stages the E and A values obtained from the Coats–Redfern equation are in good agreement with the E and A values obtained for the R_2 mechanism based on a phase-boundary reaction, cylindrical symmetry. The E value obtained from Rogers' equation using DSC data is also in fairly good agreement with this.

The E and A values obtained by the different methods show good agreement. In general, the values obtained from TG are more accurate than values from DSC experiments owing to the greater accuracy in the measurements of mass.

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