

Kinetics of Thermal Degradation of Lanthanum Complexes

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Abstract:

The kinetics and mechanism of the thermal decomposition of naphthoate complexes of lanthanum with hydrazine base have been studied by Thermal analysis techniques. The kinetic parameters for the decomposition stages (stages I and II) were calculated using the Coats Redfern equation. It is observed that there is no regular variation in the values of the kinetic parameters of decomposition of the complexes. Entropy of activation found to be positive in most of the complexes indicate the activated complexes have a less ordered structure than the reactant.

Keywords

Coats-Redfern; Activation Energy; Kinetics; Lanthanum complex

1. Introduction

All the well characterized decomposition stages of the compounds are selected for the study of the kinetics of decomposition. The kinetic parameters like the activation energy (E), the pre-exponential factor (A) and entropy of activation for the well defined stages of decomposition are calculated using Coats-Redfern equation [1]. The goodness of fit is verified by calculating the correlation coefficient. The correct order of the reaction is also found. A comparative study of various stages of decomposition can be made.

Thermogravimetric analysis (TGA) is widely used for rapidly assessing the thermal stability of various substances. A number of researchers have demonstrated its usefulness. Several methods have been developed to allow kinetic analysis of thermogravimetric data. Both experimental and analytical errors of kinetic data have been investigated by Sestak who has given major attention to the mathematical description of individual methods [2 & 3]. The most frequently used method of obtaining kinetic parameters from TG curves is developed [4]. It is a difference - differential method and attempts to determine both

the reaction and activation energy. The method has several disadvantages and often leads to uncertain or meaningless values for the order of reaction [5].

Coats and Redfern developed an integral method which is applied to TG data [1]. The correct order is assumed to lead to the best linear plot from which activation energy (E) is also determined.

2. Mechanism

General mechanism proposed for solid state reactions can be written in the form

$$\frac{d\alpha}{dT} = k.f(\alpha) \quad (1)$$

where α is the fraction reacted in time t , and k is the rate constant which depends on the absolute temperature, T .

According to the Arrhenius equation,

$$K = Ae^{-\frac{E}{RT}} \quad (2)$$

where A , E and R are constants known as the pre-exponential factor, the activation energy and the gas constant, respectively.

Since temperature increases linearly with time, then

$$T = T_0 + \phi T \quad (3)$$

where T_0 is the temperature commencement of determination and ϕ is the heating rate defined by the relation,

$$\frac{dT}{dt} = \phi \quad (4)$$

From Equations 6.1, 6.2 and 6.4 the following equation is obtained.

$$\frac{dT}{dt} = \left(\frac{A}{\phi}\right) e^{-\frac{E}{RT}} \cdot f(\alpha) \quad (5)$$

On arrangement of Equation (6.5), it gives

$$\left(\frac{1}{f(\alpha)}\right) d\alpha = \left(\frac{A}{\phi}\right) e^{-\frac{E}{RT}} \cdot dT \quad (6)$$

For general degradation reaction,



It can be written as,

$$\frac{d\alpha}{dT} = k \cdot (1-\alpha)^n \quad (7)$$

Assuming that the general relationship in homogeneous kinetics holds good for heterogeneous kinetics also. Equation (7) can also be converted by incorporating Arrhenius equation as,

$$\left(\frac{1}{(1-\alpha)^n}\right) d\alpha = \left(\frac{A}{\phi}\right) e^{-\frac{E}{RT}} \cdot dT \quad (8)$$

On integration between the limits 0 to α ,

$$\int_0^\alpha \frac{1}{(1-\alpha)^n} \cdot d\alpha = \int_0^\alpha \left(\frac{A}{\phi}\right) e^{-\frac{E}{RT}} \cdot dT$$

$$\begin{aligned} LHS &= \int_0^\alpha \frac{1}{(1-\alpha)^n} \cdot d\alpha \\ &= \frac{1-(1-\alpha)^{n-1}}{(1-n)} \quad (9) \end{aligned}$$

$$\begin{aligned} RHS &= \int_0^\alpha \left(\frac{A}{\phi}\right) e^{-\frac{E}{RT}} \cdot dT \\ &= \left(\frac{A}{\phi}\right) \int_0^\alpha e^{-\frac{E}{RT}} \cdot dT \end{aligned}$$

Using Rainville function [6],

$$RHS = \frac{AR}{\phi E} \left[1 - \frac{2RT}{E}\right] T^2 \cdot e^{-\frac{E}{RT}} \quad (10)$$

Equations (9) and (10) are equal. Hence it can be written

as

$$\frac{1-(1-\alpha)^{n-1}}{1-n} = \frac{AR}{\phi E} \left[1 - \frac{2RT}{E}\right] T^2 \cdot e^{-\frac{E}{RT}}$$

Taking log on both sides

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

This is Coats-Redfern equation

$$\text{Plotting } \left[\frac{1-(1-\alpha)^{n-1}}{(1-n)T^2} \right] \text{ vs } \frac{1}{T} \text{ gives a}$$

straight line for a parameter, n. From the slope and intercept, E and A are calculated.

3. Computation of Kinetic Parameters

Kinetic parameters of lanthanide complexes have been evaluated using the above equation (11). Figure 1 shows the well defined stages of dehydration and decomposition of [La(N₂H₄)(1-C₁₀H₇COO)₃].2H₂O complex of 1-naphthoic acid. Table 1 show the various calculated values using the equations for lanthanide metal complexes of 1-naphthoic acid.

Table. 1 Kinetic parameters of lanthanide metal complexes of 1-naphthoic acid and hydrazine

Molecular formula of the complex	Reaction	E _a in KJ/mole	A (s ⁻¹)	ΔS in KJ/kelvin
[La(N ₂ H ₄)(1-C ₁₀ H ₇ COO) ₃].2H ₂ O	Dehydration	10.11	5.52x10 ⁸	0.0181
	Decomposition	14.85	5.92x10 ⁷	0.0230
[Ce(N ₂ H ₄)(1-C ₁₀ H ₇ COO) ₃].2H ₂ O	Dehydration	19.46	13.66x10 ⁶	0.0723
	Decomposition	14.66	10.85 x10 ²	0.0814
[Pr(N ₂ H ₄)(1-C ₁₀ H ₇ COO) ₃].2H ₂ O	Dehydration	22.49	1.33x10 ⁵	0.0403
	Decomposition	58.45	6.61x10 ²	0.0662
[Nd(N ₂ H ₄)(1-C ₁₀ H ₇ COO) ₃].H ₂ O	Dehydration	16.54	1.84x10 ¹²	0.0221
	Decomposition	31.34	2.61x10 ⁶	0.0349
[Gd(N ₂ H ₄)(1-C ₁₀ H ₇ COO) ₃].H ₂ O	Dehydration	12.72	12.68x10 ⁷	0.0043
	Decomposition	10.70	10.47x10 ⁷	0.0065

It is observed from the calculated parameters of inner transition metal complexes of 1-naphthoic acid that the entropy of activation of

the second stage is found to be greater than that of the first stage in all the complexes. These values suggest that the activated complex has a less ordered structure than the reactants [7]. There is no significant trend is followed in the values of A, E and n.

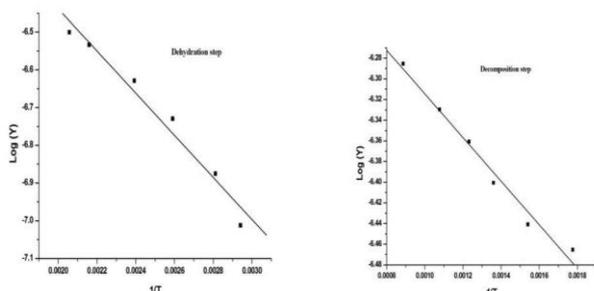


Table 2 Kinetic parameters of inner transition complexes of 2-naphthoic acid and hydrazine

Molecular formula of the complex	Reaction	E _a in KJ/mole	A (s ⁻¹)	ΔS in KJ/kelvin
[La(N ₂ H ₄) ₂ (2-C ₁₀ H ₇ COO) ₃].2H ₂ O	Dehydration	13.69	11.03x10 ⁵	0.0562
	Decomposition	15.01	1.06x10 ⁹	0.0497
[Ce(N ₂ H ₄) ₂ (2-C ₁₀ H ₇ COO) ₃].2H ₂ O	Dehydration	13.33	1.66x10 ⁷	0.0231
	Decomposition	23.24	2.94x10 ⁶	0.0316
[Pr(N ₂ H ₄) ₂ (2-C ₁₀ H ₇ COO) ₃].2H ₂ O	Dehydration	11.79	1.89x10 ⁹	0.0678
	Decomposition	20.18	1.13x10 ⁹	0.0492
[Nd(N ₂ H ₄) ₂ (2-C ₁₀ H ₇ COO) ₃].2H ₂ O	Dehydration	12.09	21.54x10 ⁸	0.0704
	Decomposition	23.58	3.59x10 ⁹	0.0562
[Gd(N ₂ H ₄) ₂ (2-C ₁₀ H ₇ COO) ₃].2H ₂ O	Dehydration	15.16	25.11x10 ⁵	0.0532
	Decomposition	34.37	48.64x10 ⁵	0.0568

The dehydration and decomposition steps of [Nd(N₂H₄)₂(2-C₁₀H₇COO)₃].2H₂O complex are shown in Figure 2. The kinetic parameters of inner transition metal complexes of 2-naphthoic acid are shown in Table 2.

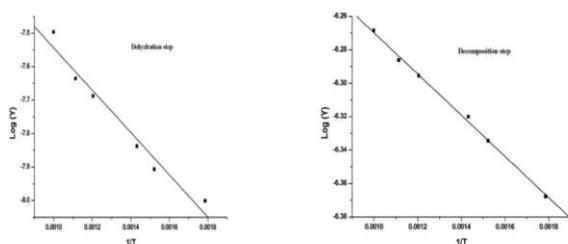


Figure.2 Dehydration and Decomposition kinetics of [Nd(N₂H₄)₂(2-C₁₀H₇COO)₃].2H₂O

Table. 3 Kinetic parameters of lanthanide metal complexes of 2-naphthoxy acetic acid and hydrazine

Molecular formula of the complex	Reaction	E _a in KJ/mole	A (s ⁻¹)	ΔS in KJ/kelvin
[La(N ₂ H ₄) ₂ (2-C ₁₀ H ₇ OCH ₂ (COO)) ₃].3H ₂ O	Dehydration	14.85	5.08x10 ⁵	0.0589
	Decomposition	54.15	8.30x10 ⁵	0.0724
[Ce(N ₂ H ₄) ₂ (2-C ₁₀ H ₇ OCH ₂ (COO)) ₃].3H ₂ O	Dehydration	13.53	3.56x10 ⁷	0.0254
	Decomposition	46.65	8.38x10 ⁴	0.0490
[Pr(N ₂ H ₄) ₂ (2-C ₁₀ H ₇ OCH ₂ (COO)) ₃].2H ₂ O	Dehydration	26.29	3.42x10 ⁵	0.0246
	Decomposition	82.54	3.44x10 ⁷	0.0385
[Nd(N ₂ H ₄) ₂ (2-C ₁₀ H ₇ OCH ₂ (COO)) ₃].3H ₂ O	Dehydration	22.17	12.17x10 ³	0.0723
	Decomposition	34.74	49.08x10 ⁷	0.0879
[Gd(N ₂ H ₄) ₂ (2-C ₁₀ H ₇ OCH ₂ (COO)) ₃].2H ₂ O	Dehydration	15.54	1.84x10 ⁶	0.0264
	Decomposition	31.34	46.6x10 ⁵	0.0568

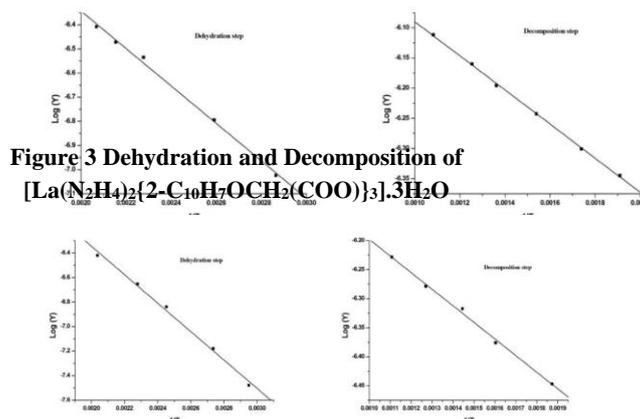


Figure 3 Dehydration and Decomposition of [La(N₂H₄)₂(2-C₁₀H₇OCH₂(COO))₃].3H₂O

Figure 4 Dehydration and Decomposition of [Nd(N₂H₄)₂(2-C₁₀H₇OCH₂(COO))₃].3H₂O

4. CONCLUSION

On the basis of the activation energy values it is found that all the complexes show similar type of decomposition reactions.

From the computational values derived from thermogravimetry it is found that energy of activation (E) values are ranging from 10.11- 82.4 KJ mol⁻¹ for all the lanthanide complexes. The higher value of E suggests higher stability of these complexes [8].

Entropy of activation found to be positive in most of the complexes indicate the activated complexes have a less ordered structure than the reactant and the reactions may be described as faster than normal in these decomposition stages.

4. References

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