

Kinetics of thermal decomposition of binary complexes of rare earth metals with some biologically relevant ligands

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Abstract: The thermal decomposition of some trivalent lanthanide complexes with crotonic acid, furan-2-carboxylic acid, meso-2,3-dimercaptosuccinic acid and sarcosine was studied by thermogravimetry under non isothermal heating conditions. The pyrolysis experiments were performed at heating rate of 10⁰C/min in an inert atmosphere of nitrogen. The kinetic analysis of the thermogravimetric data was performed by using the Coats-Redfern method and J. Zasko method. The results indicate that the values of the kinetic parameters obtained by these different methods agree well.

Keywords: Thermal decomposition; Thermogravimetry; Pyrolysis; Kinetic analysis; Coats-Redfern method; Zasko method.

Introduction

Lanthanide materials exhibit a wide variety of fascinating electrical, optical, and magnetic properties that make them ideally suited for a diverse range of applications. There is limited reference in literature regarding differential thermal analysis and thermogravimetric studies of such complexes [1- 3]. Keeping in view the importance of the biorelevant ligands, it was thought interesting to study the thermogravimetric analysis and the kinetics of thermal decomposition of the lanthanide (III) complex.

Thermogravimetry (TG) is one of the oldest thermal analytical procedures and has been extensively used to study the kinetics of decomposition reactions and calculating the kinetic parameters like activation energy (E), order of kinetics of reaction (n), pre-exponential factor (log Z) and entropies (S*)[4-13]. The thermal techniques have been demonstrating several applications: thermal characterization, study of drugs stability, preformulation studies, as well as measure the vapor pressure of substances [14].

Thermogravimetric analysis measures weight changes in a material as a function of temperature or time under a controlled atmosphere. Many methods are developed for deriving kinetic data from TG curves. In the present work, kinetic parameters were calculated for some trivalent lanthanide complexes with crotonic acid, furan-2-carboxylic acid and sarcosine using the Coats-Redfern method and J. Zasko method.

Experimental

Material

Crotonic acid (C.D.H.), Furan-2-carboxylic acid (Merck) lanthanides (Indian Rare Earths Ltd) and other chemicals of A.R., B.D.H. and Merck were used.

The solid complexes of trivalent lanthanide complexes with crotonic acid, furan-2-carboxylic acid, meso-2,3-dimercaptosuccinic acid and sarcosine were isolated from the mixture of equimolar solutions of metal

nitrate and ligands. The pH of the mixture was adjusted to 7 by adding dilute solution of KOH. The mixture was refluxed in ethanol (15-20 ml) for 3-4 hours on a steam bath. The clear solution gave a solid mass on cooling, which was filtered through G4 glass crucible and washed several times with the mixture of doubly distilled water and alcohol. It was recrystallised to give pure crystal and then dried at 60^o-70^oC

Thermal measurements

Thermal characterization of complexes was carried out using a thermal analyzer system at a heating rate of 10^oC/min in an inert atmosphere of nitrogen. The weight variation of sample was recorded as a function of sample temperature.

Results and Discussion

The complexes formed are stable at room temperature. The elemental analyses were satisfactory, show that the complexes have a metal to ligand ratio of 1:1. (Table-1)

Table 1 – The analytical data of ligand and its complexes

Compound	Mol. Wt.	Analytical data (%) Found (calculated)				
		C	H	N	S	M
CA	86.09	54.72 (55.46)	6.42 (6.86)	-	-	-
Sarcosine	89.09	41.23 (40.48)	7.12 (7.75)	15.03 (15.61)	-	-
2-FCA	112.08	52.78 (53.33)	4.12 (3.86)	-	-	-
DMSA	182.22	27.45 (26.17)	3.29 (3.19)	-	34.19 (34.97)	-
Gd-CA	243.34	19.74 (19.34)	2.46 (2.42)	-	-	64.62 (64.68)
Gd-Sarcosine	246.35	14.62 (14.52)	2.84 (2.64)	5.68 (5.32)	-	63.83 (63.63)
La-2-FCA	250.98	23.92 23.89	1.59 (1.79)	-	-	55.34 (55.16)
Gd-DMSA	339.47	14.13 (14.03)	1.76 (1.64)	-	18.88 (18.59)	46.32 (46.03)
Sm-DMSA	332.58	14.43 (14.34)	1.80 (1.69)	-	19.27 (19.15)	45.21 (45.02)

Coats and Redfern Method

In the reaction $aA(s) \rightarrow bB(s) + cC(g)$ the rate of disappearance of A may be expressed by :

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

where α = fraction of A decomposed at time 't', n = order of reaction, and k = rate constant given by the expression

$$k = Ae^{-E/RT} \quad (2)$$

where A = frequency factor, and E = activation energy of the reaction.

For a linear heating rate $a = \frac{dT}{dt}$ Coats and Redfern used the following relationships.

$$\log F(\alpha) = \log \left[\frac{1 - (1 - \alpha)^{1-n}}{T^2(1-n)} \right] = \log \frac{AR}{aE} \left[1 - \frac{2RT}{E} \right] - \frac{E}{2.3RT} \quad (3)$$

When $n \neq 1$ and

$$\log F(\alpha) = \log \left[\frac{-\log(1-\alpha)}{T^2} \right] = \log \frac{AR}{aE} \left[1 - \frac{2RT}{E} \right] - \frac{E}{2.3RT} \quad (4)$$

when $n = 1$

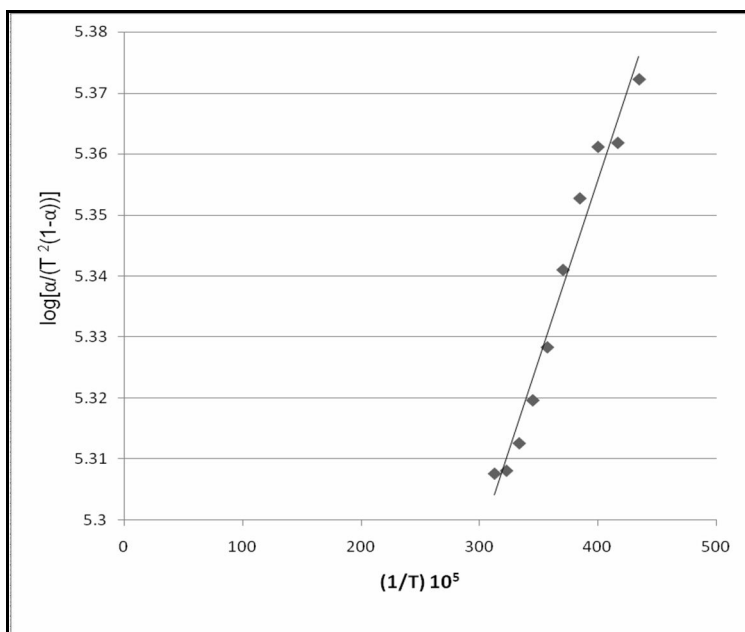


Fig. 1- Coats and Redfern type plot for Gd(III) – DMSA complex

In order to determine the kinetic parameters of the thermal decomposition of complexes the value of the function $F(\alpha)$ was calculated for the assumed reaction orders $n = \frac{1}{2}, 1, 2, 3$. Thus a plot of either $\log [1-(1-\alpha)^{1-n}/T^2(1-n)]$ against $1/T$ when $n \neq 1$ or $\log [-\log(1-\alpha)/T^2]$ against $1/T$ when $n=1$ should result in a straight line of slope $E/2.3R$ for the correct value of n . Activation energies and reaction orders calculated from the thermogravimetric data for the decomposition of complexes are presented in table 2.

Table 2 – Kinetic parameters of complexes

Studied Complexes	Studied Method	Order of Reaction	E (kcal/mol)	log Z	S*(eu)
Gd-DMSA	Zasko	2	20.00	10.9398	-2.98
	Coats and Redfern	2	12.35	-	-
Sm-DMSA	Zasko	2	12.00	9.1944	-29.33
	Coats and Redfern	2	12.07	-	-
Gd-CA	Zasko	1	14.00	10.4039	-6.39
	Coats and Redfern	1	20.92	-	-
La-2-FCA	Zasko	2	12.00	12.818	-37.50
	Coats and Redfern	2	8.69	-	-
Gd-Sarcosine	Zasko	2	12.00	9.4475	-18.79
	Coats and Redfern	2	10.42	-	-

In order to verify the determined activation energies the J. Zasko method was employed.

J. Zasko Method

The trial and error method of Doyle was modified by Zasko employing the standard deviations in the calculation instead of curve fitting procedure. Doyle's equation for thermogravimetric curves is

$$g(\alpha) = \frac{ZE}{Rq} \cdot P(x) \quad (5)$$

where $g(\alpha)$ is a certain function of α , where α stands for the fraction of initial compound reacted, Z = frequency factor, E = activation energy, R = gas constant, q = heating rate. $P(x)$, the value of integral

$$P(x) = \frac{e^{-x}}{x} - \int_x^\infty \frac{e^{-u}}{u} \cdot d\mu$$

where, $\mu = E/RT$

The main difficulty in this method is that application of this equation as $P(x)$ depends both on temperature and activation energy.

The value of α is determined by

$$\alpha = \frac{W_0 - W}{W_0 - W_t} \quad (6)$$

where W , W_0 , W_t are the actual, initial and final weight of the sample respectively. The values of $g(\alpha)$ may be calculated for various values of 'b' (order of decomposition) in a general equation

$$\frac{d\alpha}{dt} = K(1 - \alpha)^b \quad (7)$$

where values for 'b' are considered as 0, 1 and 2 when

$$b = 0 : g_0(\alpha) = \alpha \quad (8)$$

$$b = 1 : g_1(\alpha) = \ln(1 - \alpha) \quad (9)$$

$$b = 2 : g_2(\alpha) = \frac{\alpha}{1 - \alpha} \quad (10)$$

If the logarithm of equation (1) is taken then

$$\log \frac{ZE}{Rq} = \log g(\alpha) - \log P(x) = B \quad (11)$$

The values of integral

$$P(x) = \frac{e^{-x}}{x} - \int_x^\infty \frac{e^{-u}}{u} \cdot d\mu \quad (12)$$

were calculated and tabulated by Doyle for 'x' values covering a range from 10 to 50 and these values were used in calculating 'B' in equation (7)

$$B_0 = \log g_0(\alpha) - \log P(x) \quad (13)$$

$$B_1 = \log g_1(\alpha) - \log P(x) \quad (14)$$

$$B_2 = \log g_2(\alpha) - \log P(x) \quad (15)$$

The $-\log P(x)$ were taken corresponding to over a range of 10 to 24 E values.

The average of 'B' values as obtained at different values of E and at different temperature was taken and their ' δ ' values have been determined employing the relation for standard deviation

$$\delta = \sqrt{\frac{(B_1 - \bar{B})^2}{r}} \quad (16)$$

Where 'B₁' is any value, \bar{B} is the arithmetic mean, 'r' is the number of values.

The 'δ' values at a particular temperature is minimum for a particular 'b' value i.e. the apparent reaction order using interpolated $-\log p(x)$ at each temperature, the 'δ' values have been calculated for E values in a close range. The correct value for E_a gives minimum 'δ' value at the particular 'b'.

The apparent frequency factor 'Z' is calculated by the equation

$$\text{Log } Z = \bar{B} + \log Rq - \log E \quad (17)$$

And the apparent activation entropy as

$$S^* = 2.303 \log \frac{Zh}{KT} \quad (18)$$

The value of T is taken as temperature (T_{1/2}) at which the weight loss is half of the total weight loss during the considered step.

Conclusion

Activation energies and reaction orders for the decomposition of complexes calculated from the thermogravimetric curves using the Coats-Redfern method and J. Zasko method show satisfactory agreement.

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