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KINETICS AND MECHANISM OF THE THERMAL DECOMPOSITION OF LANTHANUM COMPLEXES OF NAPHTHOATE WITH HYDRAZINE

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Abstract*— The kinetics and mechanism of the thermal decomposition of naphthoate complexes of lanthanum with hydrazine have been explained by thermal analysis. In kinetic studies the major decomposition stages (stages I and II) were calculated using the Coats Redfern equation. The TG and DTA data indicated that all complexes are thermo stable up to 91.9 K. The thermal decomposition of all Ln(III) complexes was a three-stage process except lanthanum 2- hydroxy 1- naphthoic acid and La_2O_3 as a final product for all the complexes. The activation energies of thermal decomposition of the complexes were calculated from analysis of the TG-DTA curves using the Coats Redfern methods.

Keywords*— Coats-Redfern; Kinetics; Lanthanum; Decomposition; Thermal decomposition

I. INTRODUCTION

Lanthanide complexes have been widely used in fluorescent, sensors and magnetic resonance imaging etc. [1,2]. The hexagonal structure phase of La_2O_3 is stable up to 2050 °C. It is an important component of automobile exhaust gas conversion and it is a catalyst support in the formation of gas conversion catalyst [3]. Thermogravimetry is the one of the oldest method to provide the information about the sample composition, thermal stability as well as the kinetic data relating the chemical changes occur on heating [2]. In the present work, we studied the thermogravimetric analysis and the kinetics of the thermal decomposition of the napthoate complexes of lanthanum with hydrazine.

II. EXPERIMENTAL

Preparation of $[La(N_2H_4)\{1/2\text{-}C_{10}H_7(COO)\}_3].2H_2O$ & $[La(N_2H_4)_2\{C_{10}H_6(1/2\text{-}O)(2/1\text{-}COO)\}_{1.5}].nH_2O$ where n = 0 & 3

Lanthanum oxide (0.325g, 1mmol) was dissolved in a minimum quantity of 1:1 HNO_3, evaporated to eliminate excess of acid, and dissolved in 20 mL of water. This was added slowly to a freshly prepared aqueous solution (60 mL) of the ligand containing naphthoic and hydroxyl naphthoic acid (0.188 g, 1 mmol) and hydrazine hydrate (0.2 g, 4 mmol) at 70 °C, stirring the reaction mixture at pH 6. Immediately turbidity developed which turned out to be micro-crystalline solid. Crystalline product obtained was washed with water, alcohol and then with ether and dried in a desiccators over anhydrous $CaCl_2$. A similar procedure was adopted for obtaining the other lanthanides with the molar ratio Metal: Acid: Base =1:1:4.

The simultaneous TG-DTA studies were done on a STA 1500 thermal analyzer, NETZSCH-Geratebeau GmbH thermal analyzer and the curves obtained in air using platinum cups as sample holders with 5-10 mg of the samples at the heating rate of 10 ºC/min. in O_2/air atmosphere up to 700-900 ºC.

III. RESULT AND DISCUSSION

The elemental analysis, Thermal analysis, magnetic moments, infrared and electronic and spectra show that the five complexes have the formulae: $[La(N_2H_4)(1\text{-}C_{10}H_7COO)_3].2H_2O$, $[La(N_2H_4)_2(2\text{-}C_{10}H_7COO)_3].2H_2O$, $[La(N_2H_4)_2\{C_{10}H_6(1\text{-}O)(2\text{-}COO)\}_{1.5}].3H_2O$, $[La(N_2H_4)_2\{C_{10}H_6(2\text{-}O)(1\text{-}COO)\}_{1.5}]$. The hydrazine acts as a neutral bidentate ligand coordinating to the central metal ion. The compositions of the intermediate and the final products are those which best fit with the observed weight loss in the TG studies. Thermogravimetric results are in good agreement with the DTA data. The TG and DTA curves of all four complexes are given in Figs. 1-4. Simultaneous TG-DTA data of the naphthoate and hydroxy naphthoate complexes are summarized in Table.1.

The hydrated complex of Lanthanum 1- naphthoate $[La(N_2H_4)\{1\text{-}C_{10}H_7(COO)\}_3].2H_2O$ is thermally stable up to 99 °C and undergoes decomposition into three stages (Table 1) as represented by the DTA peaks at 91.9, 269 and 654 °C. The first stage of endothermic dehydration corresponds to a weight loss of 7.1%, which may be attributed to the loss of two molecules of water. The second stage with a mass loss of 26.7 % may be due to the exothermic decomposition of $La(N_2H_4)\{1\text{-}C_{10}H_7(COO)\}_3$ in to unstable oxy carbonate intermediate $[La_2O_2CO_3]$ (4). The third stage intermediate oxy

carbonate decomposition in to lanthanum oxide and the corresponding weight loss is 50.3%. The decomposition temperatures of these intermediates agree with the values reported.

In Lanthanum 2- naphthoate complex $[La(N_2H_4)\{2\text{-}C_{10}H_7(COO)\}_3].2H_2O$ undergoes decomposition in three stages giving the stable lanthanum oxide as the final residue. In the first step of endothermic decomposition starts at about 75 °C to form $[La(N_2H_4)\{2\text{-}C_{10}H_7(COO)\}_3]$ and the corresponding weight loss of 5.2%, implying loosely bound lattice water. In the second step weight loss (9.3%) is due to the formation of unstable intermediate $[La\{2\text{-}C_{10}H_7(COO)\}_3]$ showing exotherms decomposition in the range 149-225. The final step of decomposition occurs with a weight loss of 79.4% which may be due to the decomposition of intermediate to metal oxide. The formation of final products was confirmed their pXRD patterns.

The thermal analysis of Lanthanum complex of 1- hydroxy -2-naphthoic acid evinces the decomposition in three stages. The hydrated complexes of 1 - hydroxy - 2- naphthoates are stable in air upto 75 °C, and are then dehydrated by showing endothermic peaks in the temperature range of 75 - 149 °C and the weight loss is 10.1%, followed by decomposition in the second step forming an unstable intermediate, probably $La_2(C_2O_4)_3$,with a display of an exothermic peak in the range of 228-600 °C in DTA . During last step of decomposition of the complexes (weight loss 67%), the intermediate degrades to the respective metal oxide showing a strong exothermic peak in the range of 600-800 °C.

Lanthanum 2- hydroxy -1-naphthoate complex $[La(N_2H_4)_2\{C_{10}H_6(2\text{-}O)(1\text{-}COO)\}_{1.5}]$ undergoes decomposition in four stages as indicated by the DTA peaks obtained at 85 , 426, 580 and 675 °C (5) and weight loss corresponds to 13.3, 57.1, 61.7 and 66.3% respectively. In the second and third stage unstable intermediate $[La_2O(CO_3)_2]$ and $[La_2O_2CO_3]$ are formed [6]. In the final stage this intermediate undergoes exothermic decomposition to form corresponding metal oxide as final product.

From the thermal studies, the nature of the decomposition changes with the anion, even though all the complexes contain same ligand. Except 2-hydroxy -1-naphthoic acid all the complexes show two stage decompositions. In all the complexes of lanthanum contain two bridged hydrazine molecules and bidentate nature of carboxylate ions present in inside the coordination sphere. Hence, their thermal stability is more or less the same. The thermal stabilities of the naphthoic acid complexes are less than those of the hydroxy naphthoic acid complexes, because the strain at the central atom is more in hydroxy naphthoic acid complexes.

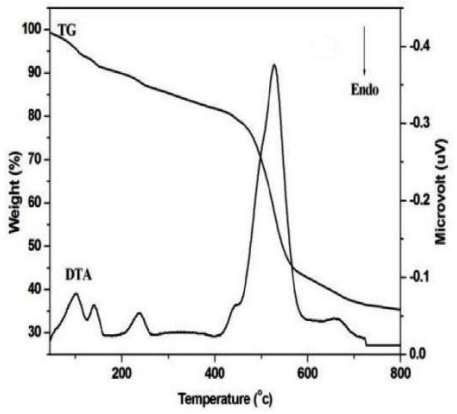

Fig. I. TG and DTA curves of $[La(N_2H_4)(1\text{-}C_{10}H_7COO)_3].2H_2O$ complex.

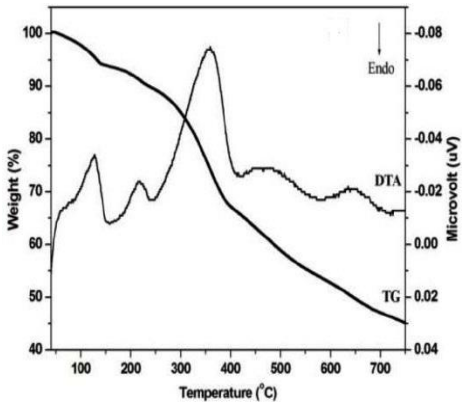

Fig. 2. TG and DTA curves of $[La(N_2H_4)_2(2\text{-}C_{10}H_7COO)_3].2H_2O$ complex

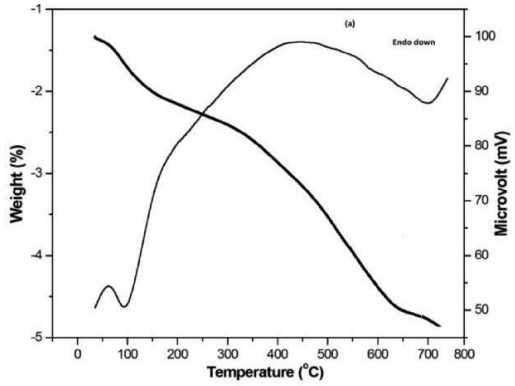

Fig. 3. TG and DTA curves of $[La(N_2H_4)_2\{C_{10}H_6(1\text{-}O)\ (2\text{-}COO)\}_{1.5}].3H_2O$ complex

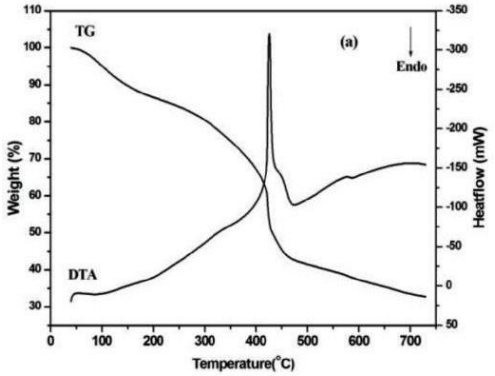

Fig. 4. TG and DTA curves of $[La(N_2H_4)_2\{C_{10}H_6(2\text{-}O)(1\text{-}COO)\}_{1.5}]$ complex

Table 1 Thermal analysis data of Lanthanum naphthoate & Hydroxy naphthoate complexes

Molecular formula of the complexes	DTA peak Temp (°C)	TG			Intermediate/End product
		Temp. Range (°C)	Observed	Calculated	
$[La(N_2H_4)\{1\text{-}C_{10}H_7(COO)\}_3].2H_2O$	91.9(+) 269(-) 520(-) 654(-)	99-200 200-450 450-700	7.1 26.1 50.4	7.4 26.2 50.3	$[La(N_2H_4)\{1\text{-}C_{10}H_7(COO)\}_3]$ $[La_2O_2CO_3]$ La_2O_3
$[La(N_2H_4)\{2\text{-}C_{10}H_7(COO)\}_3].2H_2O$	127(+) 216(-) 358(-) 643(-)	75-149 149-225 225-700	5.3 9.4 79.3	5.2 9.3 79.4	$[La(N_2H_4)\{2\text{-}C_{10}H_7(COO)\}_3]$ $[La\{2\text{-}C_{10}H_7(COO)\}_3]$ La_2O_3
$[La(N_2H_4)_2\{C_{10}H_6(1\text{-}O)(2\text{-}COO)\}_{1.5}].3H_2O$	102(+) 350(-) 710(+)	65-228 228-600 600-800	10.2 48.9 66.8	10.1 49.0 67.0	$[La(N_2H_4)_2\{C_{10}H_6(1\text{-}O)(2\text{-}COO)\}_{1.5}]$ $La_2(C_2O_4)_3$ La_2O_3
$[La(N_2H_4)_2\{C_{10}H_6(2\text{-}O)(1\text{-}COO)\}_{1.5}]$	85 (+) 426 (-) 580(-) 675(-)	65-150 150-460 460-600 600-721	13.2 56.9 62 66	13.3 57.1 61.7 66.3	$[La\{C_{10}H_6(2\text{-}O)(1\text{-}COO)\}_{1.5}]$ $[La_2O(CO_3)_2]$ $[La_2O_2CO_3]$ La_2O_3

Computation of Kinetic Parameters

The kinetic studies of the thermal decomposition of the lanthanum complexes were carried out using a computer program. Dehydration and decomposition were selected for the study of the kinetics of decomposition of the complexes. Coats and Redfern developed an integral method which is applied to TG data [7]. The correct order is assumed to lead to the best linear plot from which activation energy (E) is also determined. Coats and Redfern equation is

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

Plotting $\left[\frac{1-(1-\alpha)^{n-1}}{(1-n)T^2}\right] vs \frac{1}{T}$ gives a straight line for a parameter, n

From the slope and intercept, E and A are calculated.

The best of fit was assessment by correlation coefficient method. The entropy of activation ΔS can be calculated using the equation.

$$A=\frac{kT}{h}e_R^{\Delta S}$$

where k is Boltzmann's constant, h Planck's constant, and S the entropy of activation.

The kinetic parameters of the decomposition reactions of the complexes of lanthanum are given in Table 2. There is no regular variation carried out in the values of the kinetic parameters of decomposition of the lanthanum complexes as with other common physical constants and melting point, etc.,

The activation energy is similar with the activation energy of dehydration of the hydrated salts. This indicates that the ligands are loosely bond to the central metal ion through electrostatic forces, because 4f electrons shielded by the $5s^25p^6$ octet are not available for covalent bonding. There is no definite trend in the values of the energy of activation or the entropy of activation.

The calculated parameters of all the lanthanum of 1& 2-naphthoic acid, 1-hydroxy-2-naphthoic acid and 2-hydroxy-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 [8]. There is no significant trend is followed in the values of A, E and n.

Table 2 Kinetic parameters of the thermal decomposition of lanthanum complexes

Complex	Stages	E_a in KJ/mole	A (s^{-1})	ΔS in KJ/kelvin
$[La(N_2H_4)(1\text{-}C_{10}H_7COO)_3].2H_2O$	I	10.11	$5.52x10^8$	0.0181
	II	14.85	$5.92x10^7$	0.0230
$[La(N_2H_4)_2(2\text{-}C_{10}H_7COO)_3].2H_2O$	I	13.69	$11.03x10^5$	0.0562
	II	15.01	$1.06x10^9$	0.0497
$[La(N_2H_4)_2\{C_{10}H_6(1\text{-}O)(2\text{-}COO)\}_{1.5}].3H_2O$	I	36.2	44.23×10^7	0.0192
	II	38.2	80.92×10^{14}	0.0262
$[La(N_2H_4)_2\{C_{10}H_6(2\text{-}O)(1\text{-}COO)\}_{1.5}]$	I	10.56	$1.17\ x10^5$	0.0643
	II	11.56	$14.10x10^4$	0.0806

REFERENCES

[1] Y. Zheng, L. Fu, Y. Zhou, J. Yu, Y. Yu, S. Wang, and H. Zhang, "Electroluminescence based on a *β*-diketonate ternary samarium complex,". *Journal of Materials Chemistry*, vol.12, pp. 919–923, 2002.

[2] M. Vicente, R. Bastida, C. Lodeiro, A. Macías, A. J. Parola, L. Valencia, and S. E. Spey, "Metal complexes with a new N_4O_3 amine pendant-armed macrocyclic ligand: synthesis, characterization, crystal structures, and fluorescence studies," *Inorg.Chem.*,vol.42(21), pp. 6768-6779,2003.

[3] V. A. Murugan, S. C. Navale, and V. Ravi, **"**Synthesis of nanocrystalline La_2O_3 powder at 100 °C," *MattLett.*, Vol. 60(6), pp. 848-849, 2006.

[4] B. A. A. Balboul, A. M. Ei- Roudi, E. Samir, and A. G. Othman, "Non- isothermal studies of the decomposition course of lanthanum oxalate decahydrate," *Thermochim. Acta.* Vol. 387(2), pp.109-114, 2002.

[5] M. A. Gabal, "Non-isothermal studies for the decomposition course of CdC_2O_4-ZnC_2O_4 mixture in air," *Thermochemica. Acta*., 412, pp. 55- 62, 2004.

[6] Y. U. Zhan Gung, Jun-Xia, X. U. Zhi-gao, ZHOU Fang and CHI Ru-an, 2012, "Kinetics of thermal decomposition of lanthanum oxalate hydrate," *Trans. Nonferrous. Met. Soc. China*, 22, pp. 925 -934, 2012.

[7] A. W. Coats, and J. P. Redfern, Coats, "Kinetic Parameters from Thermogravimetric Data,"*Nature*, 201, 68-69, 1964.

[8] M. K. M. Nair, and P. K. Radhakrishnan, "Kinetics and mechanism of the thermal decomposition of lanthanum complexes of 4-*N*-(4′- antipyrylmethylidene) amino antipyrine," *Thermochim. Acta*, vol. 261, pp.141-149, 1995