FORMATION AND DISSOCIATION OF LANTHANUM COMPLEXES OF NAPHTHOATE WITH HYDRAZINE

Abstract

The hydrazine ligand and substituted naphthoic acid were used to create Praseodymium metal complexes. Coats-Redfern approach was used to calculate the kinetic parameter after studying the complexes thermal behaviour (TGA/DTA). All compounds are thermally stable up to 91.9 K, according to the TG and DTA measurements. The data from the thermo gravimetric study make it abundantly evident that the complexes decompose in two or three phases. The metal oxide was the last compound to decompose. There has been a speculative mechanism described for the heat breakdown.

Keywords: Coats-Redfern, Naphthoic acids, Thermal decomposition, Gravimetric analysis

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I. INTRODUCTION

One of the more active inorganic chemistry study areas is lanthanide coordination chemistry [1- 4]. The nature of the coordinating ligands depends on the type of polyhedron formed, with lanthanides and actinides typically having a high coordination number. Up to 2050 °C, Lanthanum metal oxide hexagonal structural phase remains stable. It serves as a catalyst support during the production of the gas conversion catalyst and is a crucial part of the conversion of car exhaust gases [3]. The development of MRI contrast agents (mainly Gd^{3+} complexes), nuclear medicine diagnostic agents, and therapeutic radiopharmaceuticals has been a major driver of interest in paramagnetic and radioactive metal ions [4].

One of the earliest methods to offer details regarding sample composition, thermal stability, and kinetic data linking and on heating, chemical changes take place in thermogravimetry [2]. In the current work, we looked at the thermal analysis and the kinetics of the thermal breakdown of lanthanum napthoate compounds with hydrazine.

II. EXPERIMENTAL PREPARATION OF $[Pr(N_2H_4)\{1\&2\text{-}C_{10}H_7(COO)\}_3].2H_2O$ & $[Pr(N_2H_4)_2\{C_{10}H_6(1\&2\text{-}O)(2\&1\text{-}COO)\}_{1.5}].nH_2O$; WHERE n = 0 & 3

A minimum of 1:1 HNO_3 was used to dissolve the praseodymium oxide (0.325g, 1mmol), after which the excess acid was evaporated and it’s dissolved in 20 mL of aqueous solution. This was gradually added while stirring the reaction mixture at pH 6 to a freshly made aqueous solution (60 mL) of the ligand that contained naphthoic and substituted naphthoic acid (0.188 g, 1 mmol), hydrazine hydrate (0.2 g, 4 mmol), and other ingredients [5]. Turbidity appeared right away and was later determined in the form of a microcrystalline solid. The resulting product was cleaned with ether, alcohol, and water before being dried in a desiccator on anhydrous $CaCl_2$. The additional lanthanides were also obtained using a similar process, using the molar ratios Metal: Acid: Base =1:1:4.

III. RESULT AND DISCUSSION

The five complexes are shown to have the formulae by the elemental analysis, thermal analysis, magnetic moments, infrared, and electronic spectra: $[Pr(N_2H_4)(1\text{-}C_{10}H_7COO)_3].2H_2O$, $[Pr(N_2H_4)_2(2\text{-}C_{10}H_7COO)_3].2H_2O$, $[Pr(N_2H_4)_2\{C_{10}H_6(1\text{-}O)(2\text{-}COO)\}_{1.5}].3H_2O$, $[Pr(N_2H_4)_2\{C_{10}H_6(2\text{-}O)(1\text{-}COO)\}_{1.5}]$. The centre metal ion is attached to a bivalent neutral ligand called hydrazine. The intermediate and final product compositions are those that correspond most closely to the weight loss shown in the TG experiments. Differential thermal analysis curves of all four compounds are given in Figs. 1- 4. Table.1 summarises the simultaneous TG-DTA data of the compounds of naphthoate and hydroxy naphthoate.

The five complexes have the following equations, according to the results of the elemental analysis, thermal analysis, magnetic moments, IR and UV spectra: $[Pr(N_2H_4)(1\text{-}C_{10}H_7COO)_3].2H_2O$, $[Pr(N_2H_4)_2(2\text{-}C_{10}H_7COO)_3].2H_2O$, $[Pr(N_2H_4)_2\{C_{10}H_6(1\text{-}O)(2\text{-}COO)\}_{1.5}].3H_2O$, $[Pr(N_2H_4)_2\{C_{10}H_6(2\text{-}O)(1\text{-}COO)\}_{1.5}]$. Hydrazine, a neutral bidentate ligand, is joined to the main metal ion. The intermediate and final product compositions are those that correspond most closely to the weight loss shown in the TG experiments. Thermogravimetric measurements and the DTA data agree well. Figs. 1-4 show the TG and

DTA curves for each of the four complexes. Table.1 summarizes the consecutive TG-DTA data of the complexes of naphthoate and hydroxy naphthoate.

Praseodymium 1-Naphthoate Hydrated Complex $[Pr(N_2H_4)\{1\text{-}C_{10}H_7(COO)\}_3].2H_2O$. The DTA peaks at 85.6, 263.9, and 657.1 °C indicate the three stages of $2H_2O$'s breakdown, which is thermally stable up to 98 °C. Weight loss of 7.3% is associated with the initial stage of endothermic dehydration and can be linked to the loss of two water molecules. The heat releasing of $Pr(N_2H_4)1\text{-}C10H_7(COO)_3$ in too unstable oxy carbonate intermediate $[Pr_2O_2CO_3]$ may be the cause of the second stage's mass loss of 25.4%.[4]. The weight loss associated with the intermediate third stage oxy carbonate breakdown into lanthanum oxide is 66.4%. These intermediates' breakdown temperatures match the values that have been reported.

In the compound $[Pr(N_2H_4)\{2\text{-}C_{10}H_7(COO)\}_3].2H_2O$ of praseodymium. Three steps of $2H_2O$ breakdown result in the stable lanthanum oxide as the final product. The first stage of endothermic breakdown begins at around 65 °C and results in the formation of $[Pr(N_2H_4)\{2\text{-}C_{10}H_7(COO)\}_3]$ and a weight loss of 5.1%, which suggests weakly attached lattice water. Weight loss of 9.8% is caused by the creation of the unstable intermediate $[Pr\{2\text{-}\ C_{10}H_7(COO)\}_3]$ in the second step, which exhibits exothermic breakdown in the range of 152-280. A weight loss of 75.4% happens in the final stage of decomposition, which may be caused by the breakdown of intermediate into metal oxide. Their pXRD patterns verified the final products' creation.

Three steps of decomposition are evident from the Praseodymium compound of 1-hydroxy-2-naphthoic acid's thermal analysis. The hydrated compound of 1-hydroxy-2-naphthoates are stable in air up to 63 °C, and then dehydrated by exhibiting endothermic peaks in the temperature range of 63 - 140 °C and the weight loss is 10.2% then decomposition is the subsequent phase, resulting in the formation of an unstable intermediate, most likely $Pr_2(C_2O_4)_3$, with a display of an exothermic peak in the temperature range of 140 The intermediate degrades to the appropriate metal oxide at the last stage of the complexes' breakdown (weight loss of 68%), showing a large exothermic peak in the temperature range of 625-790 °C.

The DTA peaks found at 70, 386, and 427 °C [6] suggest that the praseodymium 2-hydroxy-1-naphthoate compound $[Pr(N_2H_4)_2\{C_{10}H_6(2\text{-}O)(1\text{-}COO)\}_{1.5}]$ decomposes in four phases, with weight losses of 13.2, 43.2, and 64.3%, respectively. The unsteady middle $[Pr_2O(C_2O_3)_4]$ is generated in the second stage [7]. This intermediate is exothermically decomposed in the final step to produce the final product, which is the equivalent metal oxide.

Thermal studies show that, despite all complexes having the same ligand, the kind of breakdown varied with the anion. Every compound, with the exception of 2-hydroxy-1-naphthoic acid, exhibits a two-stage breakdown. Each of the praseodymium complexes has two bridging hydrazine molecules and carboxylate ions that are bidentate in nature internal to the coordination sphere. As a result, their heat tolerance is roughly the same. Because there is higher tension at the main atom in hydroxy naphthoic acid complexes, their thermal stabilities are lower than those of naphthoic acid complexes.

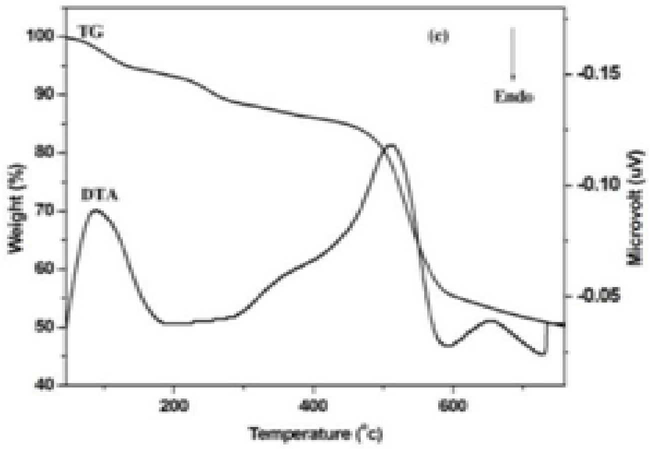

Figure 1: TG and DTA curves of [$Pr(N_2H_4)(1\text{-} C_{10}H_7COO)_3$].$2H_2O$ compound

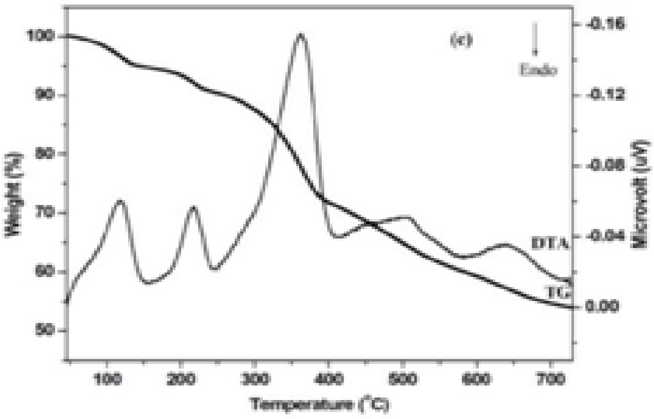

Figure 2: TG and DTA curves of [$Pr(N_2H_4)_2(2\text{-} C_{10}H_7COO)_3$].$2H_2O$ compound

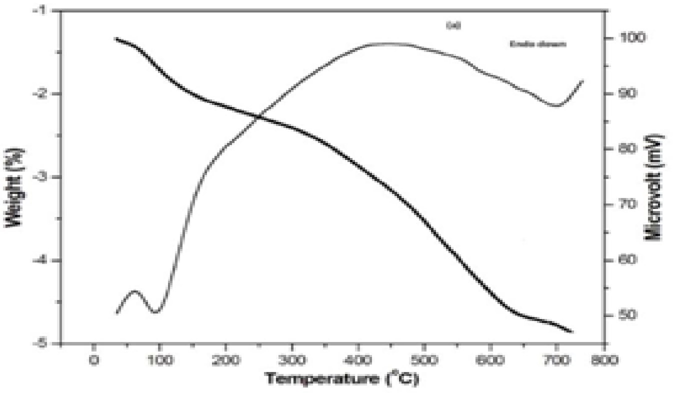

Figure 3: TG and DTA curves of curves of [$Pr(N_2H_4)_2\{C_{10}H_6(1\text{-}O)\ (2\text{-}COO)\}_{1.5}$].$3H_2O$ compound

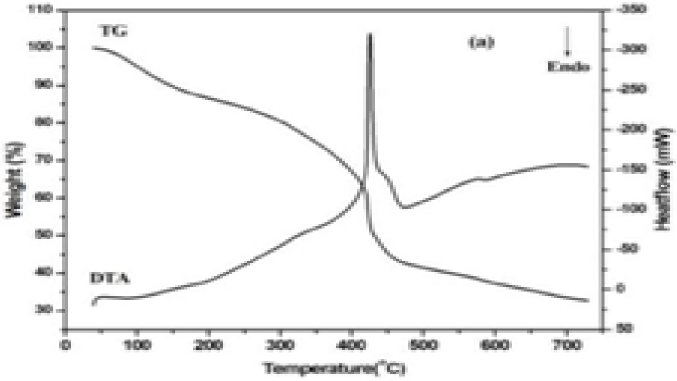

Figure 4: TG and DTA $[Pr(N_2H_4)_2\{C_{10}H_6(2\text{-}O)(1\text{-} COO)\}_{1.5}]$ compound

Table 1: Thermal analysis information for complexes of lanthanum naphthoate and hydroxy naphthoate

Compound	DTA peak Temp (°C)	TG			Intermediate/End product
		Temp. Range (°C)	Observed	Calculated	
$[Pr(N_2H_4)\{1\text{-}C_{10}H_7(COO)\}_3].2H_2O$	85.6(+) 263(-) 513(-) 657(-)	98-201 201-500 500-700	7.3 25.4 66.4	7.2 25.5 66.2	$[Pr(N_2H_4)\{1\text{-}C_{10}H_7(COO)\}_3]$ $[Pr_2O_2CO_3]$ Pr_6O_{11}
$[Pr(N_2H_4)\{2\text{-}C_{10}H_7(COO)\}_3].2H_2O$	116(+) 217(-) 364(-) 639(-)	65-152 152-280 280-730	5.0 9.7 75.3	5.1 9.8 75.4	$[Pr(N_2H_4)\{2\text{-}C_{10}H_7(COO)\}_3]$ $[Pr\{2\text{-}C_{10}H_7(COO)\}_3]$ Pr_6O_{11}
$[Pr(N_2H_4)_2\{C_{10}H_6(1\text{-}O)(2\text{-}COO)\}_{1.5}].3H_2O$	99.5(+) 350(-) 720(+)	63-140 140-625 625-790	10.1 49.2 68.1	10.2 49.3 68.4	$[Pr(N_2H_4)_2\{C_{10}H_6(1\text{-}O) (2\text{-}COO)\}_{1.5}]$ $Pr_2(C_2O_4)_3$ Pr_6O_{11}
$[Pr(N_2H_4)_2\{C_{10}H_6(2\text{-}O)(1\text{-} COO)\}_{1.5}]$	70 (+) 386 (-) 427(-)	65-353 353-430 430-700	13.2 43.2 64.9	13.1 43.0 64.2	$[Pr\{C_{10}H_6(2\text{-}O)(1\text{-}COO)\}_{1.5}]$ $[Pr_2(C_2O_3)_4]$ Pr_6O_{11}

IV. COMPUTATION OF KINETIC PARAMETERS

Computer software was used to conduct the kinetic investigations of the heat decomposition of the lanthanum compounds. In order to examine the kinetics of the complexes' decomposition, dehydration and decomposition were used. An integral technique was created by Coats and Redfern and used with TG data [8]. The most effective linear plot, based on activation energy (E) is also calculated, is predicted to be produced by following the right order. 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 $\left[\frac{1-(1-\alpha)^{n-1}}{(1-n)T^2}\right] Vs \frac{1}{T}$ ensures a parameter's straight line, n.

The values of E and A are determined from the slope and intercept. The correlation coefficient approach was used to determine the best fit. The activation's entropy S can be

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

computed using the formula. Where k is the Boltzmann constant, h is the Planck constant, and S is the activation entropy.

Table 2 lists the kinetic characteristics of the processes that break down lanthanum compounds. As opposed to other physical constants like melting point and others, the kinetic parameter values for the breakdown of lanthanum complexes do not regularly vary.

The activation energy is comparable to the activation energy required to cause the hydrated salts to dehydrate. The lack of accessible 4f electrons for covalent bonding suggests that the ligands are only weakly bound through electrostatic forces, a metal ion. There is no discernible pattern in the activation energy and entropy measurements.

According to the estimated values for each compound of 1- and 2-naphthoic acid, 1-hydroxy-2-naphthoic acid, and 2-hydroxy-1-naphthoic acid, the second stage's activation entropy is higher than the first stage's in every case. These numbers imply that the structure of the activated complex is less structured than that of the reactants [9]. The values of A, E, and n don't follow any discernible trends.

Table 2: Kinetics of lanthanum complexes' thermal degradation

Compounds	**Steps**	**E_a in KJ/mole**	**A (s^{-1})**	**ΔS in KJ/kelvin**
$[Pr(N_2H_4)(1\text{-}C_{10}H_7COO)_3].2H_2O$	I	22.49	$1.33x10^5$	0.0403
	II	58.45	$6.61x10^2$	0.0662
$[Pr(N_2H_4)_2(2\text{-}C_{10}H_7COO)_3].2H_2O$	I	11.79	$1.89x10^9$	0.0678
	II	20.18	$1.13x10^9$	0.0492
$[Pr(N_2H_4)_2\{C_{10}H_6(1\text{-}O)(2\text{-}COO)\}_{1.5}].3H_2O$	I	33.27	40.23×10^{13}	0.0189
	II	37.18	62.93×10^{15}	0.0334
$[Pr(N_2H_4)_2\{C_{10}H_6(2\text{-}O)(1\text{-}COO)\}_{1.5}]$	I	46.19	$9.12 x10^7$	0.0560
	II	52.12	$14.10x10^{42}$	0.0806

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