FORMATION AND DISSOCIATION OF LANTHANUM COMPLEXES OF NAPHTHOATE WITH HYDRAZINE

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Abstract

Praseodymium metal complexes with substituted naphthoic acid and hydrazine ligand were made. Coats-Redfern approach was used to calculate the kinetic parameter after studying the complexes thermal behaviour (TGA/DTA). All compounds are thermo 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; Kinetics; Lanthanum; Decomposition; Thermo gravimetric

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 chemical changes occur on heating is thermogravimetry [2]. We investigated the thermogravimetric analysis and the kinetics of the heat decomposition of the lanthanum napthoate complexes with hydrazine in the current work.

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 the mixture was then dissolved in 20 mL of water. 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 hydroxy naphthoic acid (0.188 g, 1 mmol), hydrazine hydrate (0.2 g, 4 mmol), and other ingredients. Turbidity appeared right away and was later determined to be micro-crystalline solid. The resulting crystalline 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.

RESULT AND DISCUSSION

The elemental analysis, Thermal analysis, magnetic moments, infrared and electronic and spectra show that the five complexes have the formulae: $[Pr(N_2H_4)(1\text{-}C_{10}H_7COO)_3].2H_2O$, $[Pr(N_2H_4)_2(2\text{-}C_{10}H_7COO)_3].2H_2O$, $[Pr(N_2H_4)_2\{C_{10}H_6(1\text{-}O)(2\text{-}COO)\}_{1.5}].3H_2O$, $[Pr(N_2H_4)_2\{C_{10}H_6(2\text{-}O)(1\text{-}COO)\}_{1.5}]$. A neutral bidentate ligand hydrazine bonded 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 five complexes have the following equations, according to the results of the elemental analysis, thermal analysis, magnetic moments, infrared analysis, and electronic spectra: $[Pr(N_2H_4)(1\text{-}C_{10}H_7COO)_3].2H_2O$, $[Pr(N_2H_4)_2(2\text{-}C_{10}H_7COO)_3].2H_2O$, $[Pr(N_2H_4)_2\{C_{10}H_6(1\text{-}O)(2\text{-}COO)\}_{1.5}].3H_2O$, $[Pr(N_2H_4)_2\{C_{10}H_6(2\text{-}O)(1\text{-}COO)\}_{1.5}]$. 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 simultaneous 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 molecules of water. The exothermic breakdown 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 third stage intermediate 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 complex of 1-hydroxy-2-naphthoic acid's thermal analysis. The hydrated complexes of 1-hydroxy-2-naphthoates are stable in air up to 63 °C, and are then dehydrated by exhibiting endothermic peaks in the temperature range of 63 - 140 °C and the weight loss is 10.2%. This is then followed by decomposition in the second step, 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 (5) suggest that the praseodymium 2- hydroxy-1-naphthoate complex $[Pr(N_2H_4)_2\{C_{10}H_6(2\text{-}O)(1\text{-}COO)\}_{1.5}]$ decomposes in four phases, with weight losses of 13.2, 43.2, and 64.3%, respectively. The unstable intermediate $[Pr_2O(C_2O_3)_4]$ is generated in the second stage [6]. 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 inside the coordination sphere.
As a result, their thermal stability is roughly the same. Because there is higher strain at the central atom in hydroxy naphthoic acid complexes, their thermal stabilities are lower than those of naphthoic acid complexes.

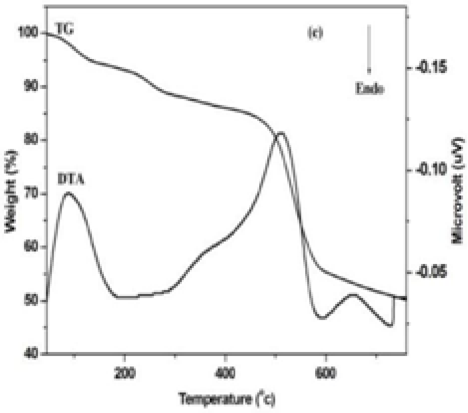

Fig. I. TG and DTA curves of

$[Pr(N_2H_4)(1\text{-}\ C_{10}H_7COO)_3].2H_2O$ complex.

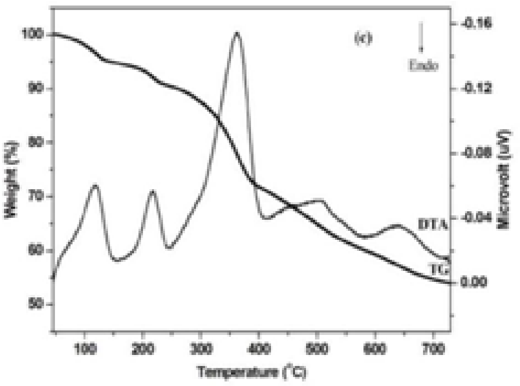

Fig. 2. TG and DTA curves of

$[Pr(N_2H_4)_2(2\text{-}\ C_{10}H_7COO)_3].2H_2O$ complex

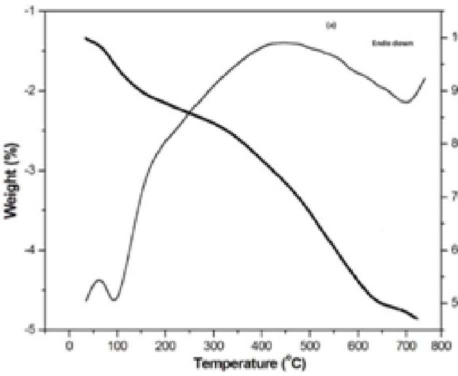

Fig. 3. TG and DTA curves of $[Pr(N_2H_4)_2\{C_{10}H_6(1\text{-}O)\ (2\text{-}COO)\}_{1.5}].3H_2O$ complex

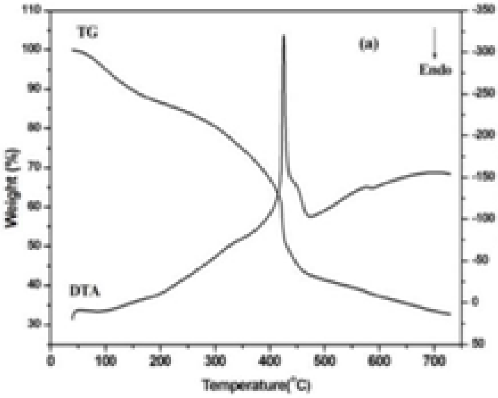

Fig. 4. TG and DTA curves of $[Pr(N_2H_4)_2\{C_{10}H_6(2\text{-}O)(1\text{-}COO)\}_{1.5}]$ complex

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	
$[Pr(N_2H_4)\{1\text{-}C_{10}H_7(COO)\}_3].2H_2O$	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	$[Pr(N_2H_4)_2\{C_{10}H_6(1\text{-}O)\ (2\text{-}COO)\}_{1.5}]$ $Pr_2(C_2O_4)$ $_3Pr_6O_{11}$
$[Pr(N_2H_4)_2\{C_{10}H_6(2\text{-}O)(1\text{-}COO)\}_{1.5}]$	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}

Computation of Kinetic Parameters

Computer software was used to conduct the kinetic investigations of the heat decomposition of the lanthanum complexes. For the study of 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 [7]. The best linear plot, from which 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 $\left[\frac{1-(1-\alpha)^{n-1}}{(1-n)T^2}\right] Vs \frac{1}{T}$ gives a straight line for a parameter, 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

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

be 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 complexes. As opposed to other common physical constants like melting point and others, the values of the kinetic parameters of the decomposition of the 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 to the core metal ion by electrostatic forces. The values of the energy of activation and the entropy of activation show no clear pattern.

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 [8]. The values of A, E, and n don't follow any discernible trends.

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**
$[Pr(N_2H_4)(1\text{- }C_{10}H_7COO)_3].2H_2O$	I	22.49	1.33×10^5	0.0403
	II	58.45	6.61×10^2	0.0662
$[Pr(N_2H_4)_2(2\text{- }C_{10}H_7COO)_3].2H_2O$	I	11.79	1.89×10^9	0.0678
	II	20.18	1.13×10^9	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	9.12×10^7	0.0560
	II	52.12	14.10×10^{42}	0.0806

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