Thermal Decomposition Studies of Lanthanide(II) Complexes with 4-Hydroxyantipyrine

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***Abstract*:** Thermogravimetric measurements of complexes of seven lanthanide(III) ions, viz., La(III), Pr(III), Nd(III), Sm(III), Gd(III), Dy(III) and Y(III) with 4-hydroxy-2,3-dimethyl-1- phenyl-3-pyrazolin-5-one (4-hydroxyantipyrine, abbreviated to hap) were recorded in dynamic air at a heating rate of 10°C min^{-1}. All the complexes are thermally stable up to ~150°C, and undergo decomposition in three stages with the removal of one hap molecule in each step with the formation of Ln_2O_3 as the final residues. Phenomenological data kinetic parameters for the thermal decomposition reactions of the complexes have been calculated from the TG data using the Coats-Redfern equation. The kinetic parameters such as order parameter, energy of activation, pre-exponential factor and entropy of activation for all the three decomposition stages of each of the complexes have been calculated.

Index Terms - Thermogravimetric analysis, 4-hydroxyantipyrine (hap), lanthanide(II) complexes, kinetic parameter.

I. INTRODUCTION

Antypyrine is an antipyretic and analgesic that has using as ear drops. Antipyrine is used as drug-metabolizing enzymes in the liver (Bottcher et al, 1982, Janus, et al 1996). In human about 40% of an antipyrine dose is oxidized to 4-hydroxyantipyrine. 4-hydroxyantipyrine is used for monitoring drug metabolism, it has also been used as a drug biodistribution promoter and a major metabolite of the drug antipyrine. 4-Hydroxyantipyrine enhances the blood-brain barrier (BBB) permeability of Antipyrine (Ohkawa et al, 2001, Remes et al, 2012). 4-Hydroxyantipyrine, which enhances the tissue-to-plasma concentration ratio of Citicoline in the brain and liver and also the thiopental sodium in the heart, liver, and brain (Ohkawa et al, 2001).

Due to the enchanting structures and properties, coordination compounds have been of greatest importance in the Chemistry field. Coordination chemistry of lanthanides is one of the active research fields in inorganic chemistry (Feng and Zhang, 2013, Kostova, 2005). The coordination compounds lanthanides are used as catalytic magnetic, luminescence, optical, electronic materials (Tsukube and Shinoda, 2002, Bünzli, 2015, Xu et al, 2015). The study of thermal properties of coordination compounds have an important role because they describe information about chemical dehydration, desolvation, thermal decomposition, heterogeneous catalysis, etc. and more over which gives the physical processes like adsorption, chemisorption, crystallization, melting, crystal transition etc. in a substance during its cooling or heating (Beuvier et al, 2015). These processes influence the properties and potential application of coordination compounds (Aspinall, 2002, Petit et al, 2015). It seems from the literature that lanthanides are capable of forming stable complexes with antipyrine and its derivatives (Al-Barody et al, 2015, Arora and Burman, 2009, Agarwal et al, 2004, Agarwal and Sarin, 1994). Regarding 4-hydroxy antipyrine complexes, there are only few studies conducted (Suresh Babu, 2001, Rijulal and Indrasenan, 2008).

Thermal analysis has wide range applications in inorganic compounds, minerals, metallic substances, ceramics, polymeric materials, pharmaceuticals substances,organic derivatives, and food related stuff and biological organisms (Duval, 1963, Ozawa, 2000). Thermogravimetry (TG) is a technique, in which the mass of asample in an environment heated or cooled at a controlled rate is measured as a function of time or temperature (Mackenzie, 1979, Hatakeyama et al, 1999). Thermal analysis is used in basic research orientated studies and numerous scientists and engineers used in various practical related applications. Thermal methods used for measuring the physical properties, thermal behavior and chemical reactions, Because of the wide range usage and applications thermal studies have greatest interest in the academic as well as in the industrial field.

II. MATERIALS AND METHODS

The nitrates of seven lanthanides (Y, La, Pr, Nd, Sm, Gd and Dy) were prepared by standard methods (Vogel, 1973). 4-Hydroxyantipyrine (99.8% pure) was purchased from Sigma-Aldrich Chemie, Germany. It was used as such as the ligand without further purification. The solvents used for the present investigation include acetone, methanol, ethanol, benzene and diethyl ether. These solvents were of either GPR or AR grade, and these were obtained commercially and purified by standard methods. Lanthanide(III) complexes with 4-hydroxyantipyrine have been synthesized and characterized by elemental analysis, molecular mass determination, molar conductance, magnetic moment measurements, FT-IR, electronic and 1HNMR spectra, and X-ray powder diffraction studies (Rijulal and Indrasenan, 2008). The TG measurements of the complexes were recorded in dynamic air at a heating rate of 10°Cmin^{-1}.

III. RESULT AND DISCUSSION

The TG/DTG/DTA curves of seven Ln(hap)$_3$ complexes are shown in Figs. 1 - 7. The detailed thermal decomposition studies given in Table 1 and Table 2.

Fig.1 TG, DTG and DTA curves of [La(hap)$_3$]

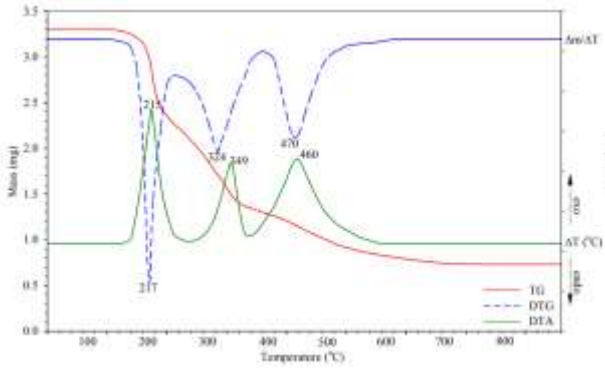

Fig.2 TG, DTG and DTA curves of [Pr(hap)$_3$]

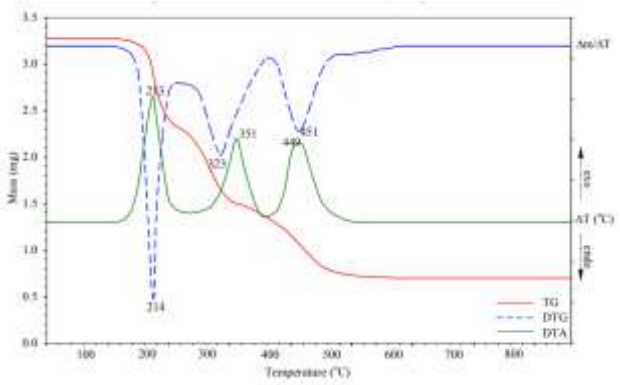

Fig.3 TG, DTG and DTA curves of [Nd(hap)$_3$]

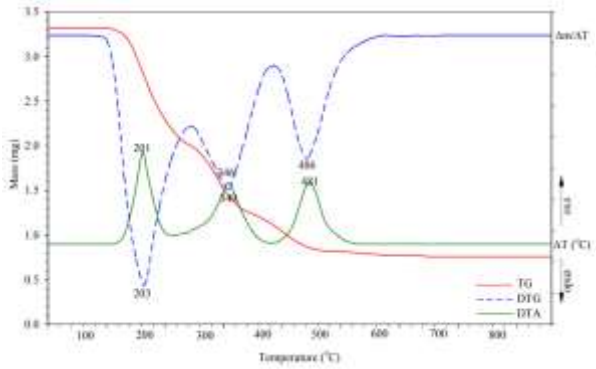

Fig.4 TG, DTG and DTA curves of [Sm(hap)$_3$]

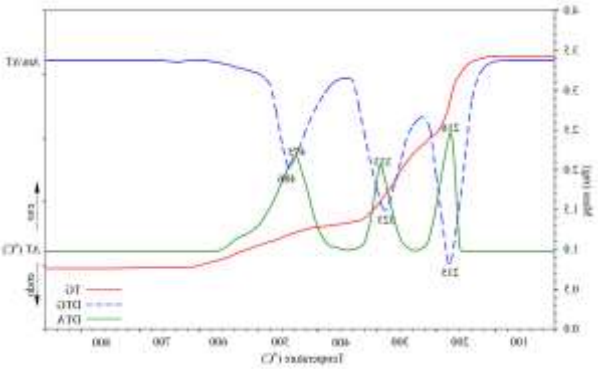

Fig.5 TG, DTG and DTA curves of [Gd(hap)$_3$]

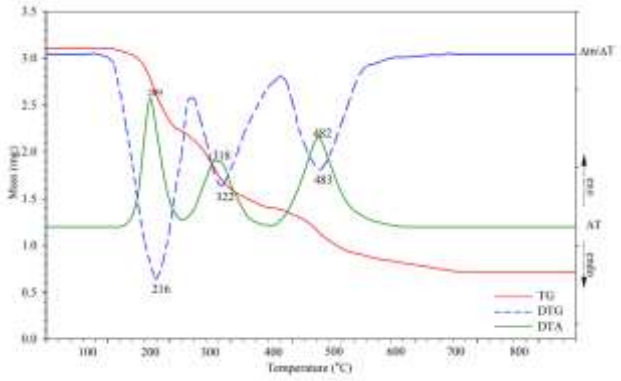

Fig.6 TG, DTG and DTA curves of [Dy(hap)$_3$]

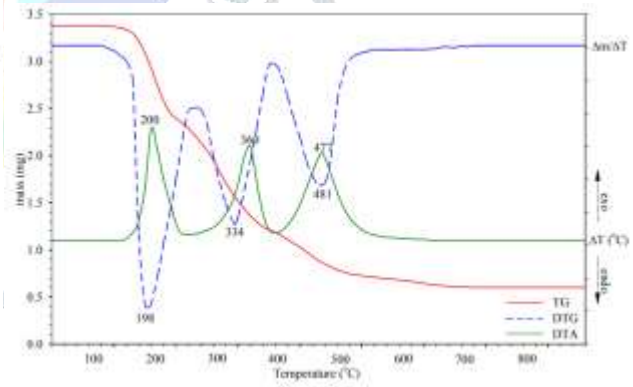

Fig.7 TG, DTG and DTA curves of [Y(hap)$_3$]

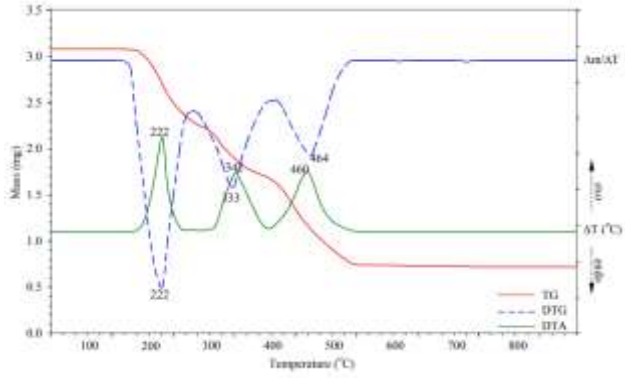

Table 1 Thermal decomposition data of lanthanide(III) complexes

Complex	Stage	Plateau in TG (^{0}C)	DTG Peak (^{0}C)	Peak width in DTG (^{0}C)	DTA Peak (^{0}C)	Mass loss (%)			Product
						TG	Pyrol.*	Cal.**	
[La(hap)$_3$]	I	Up to 160	217	180-240	215	27.3	--	27.1	[La(hap)$_2$]
	II		324	270-380	349	37.6	--	37.3	[La(hap)]
	III	After 700	470	420-530	465	77.2	78.6	78.2	La_2O_3
[Pr(hap)$_3$]	I	Up to 160	214	190-240	213	26.3	--	27.8	[Pr(hap)$_2$]
	II		323	290-390	351	37.3	--	37.1	[Pr(hap)]
	III	After 670	451	410-510	449	78.6	77.8	77.4	Pr_6O_{11}
[Nd(hap)$_3$]	I	Up to 150	215	180-250	216	27.3	--	27.0	[Nd(hap)$_2$]
	II		323	270-380	333	37.1	--	37.0	[Nd(hap)]
	III	After 680	486	420-540	475	75.8	76.2	77.7	Nd_2O_3
[Sm(hap)$_3$]	I	Up to 160	216	180-270	209	26.8	--	26.7	[Sm(hap)$_2$]
	II		322	280-420	318	35.8	--	35.9	[Sm(hap)]
	III	After 710	482	430-540	483	77.8	78.5	77.1	Sm_2O_3
[Gd(hap)$_3$]	I	Up to 150	203	160-270	201	26.8	--	26.5	[Gd(hap)$_2$]
	II		349	290-420	346	36.3	--	36.1	[Gd(hap)]
	III	After 670	486	450-550	481	75.9	76.4	76.4	Gd_2O_3
[Dy(hap)$_3$]	I	Up to 170	222	180-270	222	26.5	--	26.3	[Dy(hap)$_2$]
	II		333	280-410	342	35.4	--	35.7	[Dy(hap)]
	III	After 670	464	420-530	460	76.2	75.3	75.8	Dy_2O_3
[Y(hap)$_3$]	I	Up to 150	198	170-260	197	28.8	--	29.1	[Y(hap)$_2$]
	II		334	290-390	360	41.8	--	41.0	[Y(hap)]
	III	After 670	481	410-530	477	84.6	85.9	83.4	Y_2O_3

* Pyrolysis; **Calculated

Table 2 Kinetic parameters of thermal decomposition of lanthanide complexes

Complex	**Stage**	**Order**	**E (kJmol^{-1})**	**A (s^{-1})**	**ΔS (JK^{-1}mol^{-1})**
La(hap)$_3$	I	1.9	297.9	1.6 x 10^{30}	328.9
	II	1.6	213.6	4.1 x 10^{16}	67.2
	III	1.6	533.9	3.8 x 10^{35}	428.6
Pr(hap)$_3$	I	2.0	295.1	6.6 x 10^{29}	321.8
	II	2.0	235.9	4.1 x 10^{18}	105.6
	III	1.9	379.3	2.5 x 10^{25}	233.8
Nd(hap)$_3$	I	2.3	238.9	5.9 x 10^{23}	206.1
	II	1.7	215.9	1.2 x 10^{17}	76.3
	III	1.8	340.6	3.8 x 10^{21}	160.6
Sm(hap)$_3$	I	1.9	200.6	4.7 x 10^{19}	127.6
	II	1.3	213.8	4.3 x 10^{16}	67.8
	III	1.6	495.7	2.3 x 10^{32}	366.9
Gd(hap)$_3$	I	1.7	163.0	8.5 x 10^{15}	56.2
	II	1.7	259.8	3.5 x 10^{19}	123.2
	III	1.8	378.2	9.3 x 10^{23}	206.2
Dy(hap)$_3$	I	1.8	172.8	2.6 x 10^{16}	64.9
	II	1.5	349.2	5.0 x 10^{22}	182.1
	III	2.2	460.3	4.1 x 10^{37}	469.2
Y(hap)$_3$	I	2.1	172.4	1.5 x 10^{17}	80.2
	II	2.0	260.9	2.9 x 10^{20}	141.0
	III	1.9	740.9	1.3 x 10^{49}	687.5

Phenomenological studies

The TG curves of the lanthanum(III) complex with hap shows the plateau up to ~160ºC, and it undergoes decomposition in three stages with completion of decomposition after ~700ºC (Fig. 1). These three decomposition stages are denoted by the DTG peaks at 217, 324 and 470ºC, and the corresponding DTA peaks at 215, 349 and 465ºC. The first decomposition stage begins at 160ºC and ends at 240ºC with a mass loss of 27.3% observed in the TG curve, indicating that one of the three ligand molecules is removed as supported by the calculated mass loss value (27.1%). In the second decomposition stage one more ligand molecule is eliminated, which agrees with the mass loss obtained from the TG curve (37.6%) and the calculated mass loss value (37.3%). In the third decomposition stage the third ligand molecule is eliminated with the formation of La_2O_3 as the final residue. The total mass loss data obtained from the TG curve (77.2%) and pyrolysis experiment (78.6%) and the calculated mass loss value (78.2%). This complex is also stable up to ~160ºC, and undergoes decomposition in three stages as denoted by the DTG peaks at 214, 323 and 451ºC, and the corresponding DTA peaks at 213, 351 and 449ºC (Fig. 2). The mass loss data for these three decomposition stages obtained from the TG curve are 26.3%, 37.3% and 78.6%, which agree with the calculated mass loss values 27.8%, 37.1% and 77.4%, respectively. The final mass loss obtained from the pyrolysis experiment (77.8%) is also in agreement with the mass loss observed in the TG curve and the calculated value. The final decomposition residue obtained after ~670ºC is Pr_6O_{11}. The neodymium(III) complex is stable up to ~150ºC, and having three decomposes stages as indicated by the DTG peaks at 215, 323 and 486ºC, and the corresponding DTA peaks at 216, 333 and 475ºC (Fig. 3). As in the cases of the complexes of La(III) and Pr(III), this complex also eliminated the ligand molecules one in each step with formation of Nd_2O_3 as the final decomposition residue after ~680ºC. The mass loss data obtained from the TG curve for these three decomposition stages are 27.3%, 37.1% and 75.8%, which agree with the calculated mass loss values 27.0%, 37.0% and 77.1%, respectively. The total mass loss from the pyrolysis experiment (78.5%) also supports the formation of Nd_2O_3 as the final residue. This complex with samarium is stable up to ~160ºC, and it decomposes in three stages as indicated by the DTG peaks at 216, 322 and 482ºC, and the corresponding DTA peaks at 209, 318 and 483ºC (Fig. 4). The decomposition is complete after ~710ºC. The ligand molecules are eliminated in three stages with one molecule in each stage. This is supported by the mass loss data obtained from the TG curve for the three stages (26.8%, 35.8% and 77.8%) and the corresponding calculated mass loss values (26.7%, 35.9% and 77.1%). The total mass loss obtained from the pyrolysis experiment (78.5%) supports the formation of Sm_2O_3 as the final decomposition residue after ~710ºC. The gadolinium(III) complex decomposes in three stages as indicated by the DTG peaks at 203, 349 and 486oC, and the corresponding DTA peaks at 201, 346 and 481ºC (Fig. 5). One ligand molecule is eliminated in each step with the formation of Gd_2O_3 as the final residue. The mass loss data obtained from the TG curve (26.8%, 36.3% and 75.9%) agree with the calculated mass loss values (26.5%, 35.7% and 76.4%). $[Dy(hap)_3]$ is stable up to ~170ºC, and it undergoes decomposition in three stages as denoted by the DTG peaks at 222, 333 and 464oC, and the corresponding DTA peaks at 222, 342 and 46ºC (Fig. 6). The three ligand molecules present in the complex are eliminated one molecule in each step in conformity with the mass loss data obtained from the TG curve (26.5%, 35.4% and 76.2%) and the calculated mass loss values (26.3%, 35.7% and 75.8%). The mass loss obtained from the pyrolysis experiment (75.3%) suggests that the final residue obtained is Dy_2O_3. The yttrium(III) complex decomposes in three stages as denoted by the DTG peaks at 198, 334 and 481ºC, and the corresponding DTA peaks at 197, 360 and 477ºC (Fig 7). One of the three ligand molecules is removed in each stage with the formation of Y_2O_3 as the final residue after ~670ºC. The mass loss data observed in the TG curve (28.8%, 41.8% and 84.6%) and the calculated mass loss values (29.1%, 41.0% and 83.4%) agree with the above suggested reaction.

Kinetic studies

The kinetic parameters for the thermal decomposition reactions of the seven complexes have been calculated from the TG data using the Coats-Redfern equation (Coats and Redfern, 1964) and these values are presented in Table 1. The kinetic parameters such as order parameter, energy of activation, pre-exponential factor and entropy of activation for all the three decomposition stages of each of the complexes have been calculated. The values of order parameter fall in the range of 1.3 – 2.3 with the lowest value for the second decomposition stage of the samarium(III) complex (1.3) and the highest value for the first decomposition stage of the neodymium(III) complex (2.3). These order parameters do not have any direct relation with the thermal stability of the complexes, but they do have only the empirical significance, without which other kinetic parameters could not be evaluated using the Coats-Redfern equation. The values of energy of activation for the first decomposition stage are in the range of 163.0 - 297.9 $kJmol^{-1}$, and for the second and third decomposition stages they fall in the ranges of 213.6 - 349.2 and 340.6 - 740.9 $kJmol^{-1}$, respectively. The values of pre-exponential factor for all the three decomposition stages are in the range of $8.5x10^{15}$ - $1.3x10^{49}$ s^{-1}. The values of entropy of activation for all the decomposition stages are positive, and they are in the range of 56.2 - 687.5 $JK^{-1}mol^{-1}$.

IV. CONCLUSION

It is observed that all the seven lanthanide(III) complexes with hap undergo thermal decomposition in three stages with the elimination of one hap molecule in each step. Except $[Pr(hap)_3]$, all other lanthanide(III) complexes have Ln_2O_3 as the final residue in each case, for praseodymium(II) complex, Pr_6O_{11} is the final residue. The complexes are stable up to ~150ºC. The dysprosium(III) complex shows the maximum stability up to ~170ºC, while the yttrium(III) complex shows the least stability up to ~150ºC. The stability order of the 7 complexes in dynamic air is given as follows

$$[Dy(hap)_3] > [La(hap)_3] > [Sm(hap)_3] > [Nd(hap)_3] > [Pr(hap)_3] > [Gd(hap)_3] > [Y(hap)_3]$$
$$(170ºC) \quad (160ºC) \quad (160ºC) \quad (160ºC) \quad (160ºC) \quad (150ºC) \quad (150ºC)$$

The stability temperatures from the TG curves are given in parentheses wherever, the same TG temperatures are observed, the DTG peak temperatures are considered for deciding the stability order. The values of entropy of activation for all the decomposition stages are positive, which means the activated complexes have less ordered structures than the respective reactants (Mathew et al, 1989, Vinodkumar et al, 2000), and hence, the reactions are faster than normal.

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