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Thermal Decomposition Studies of Lanthanide (III) Complexes of NTA

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KEYWORDS

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ABSTRACT:

The thermal decomposition studies of lanthanide (III) complexes of NTA in nitrogen and air atmospheres are studied using simultaneous TG-DTA techniques with a view to compare their thermal behaviour. The phenomenological as well as kinetic aspects of thermal decomposition reactions of these complexes are discussed. The kinetic parameters for the thermal decomposition reactions are calculated. The mechanism followed in each step is provided with. The stability of the complexes in both the atmospheres is compared.

INTRODUCTION

Study of the reaction kinetics in the solid state is mainly designated to gain information about the kinetic parameters and the associated mechanism of the process. Both isothermal and non-isothermal methods have been used for the evaluation of kinetic parameters and for the elucidation of mechanism of thermal decomposition reactions. Although a wide variety of complexes of lanthanides with complexing agents have been known, It seems from literature that no successful attempts have been carried out to study the detailed kinetics of the thermal decomposition of majority of these complexes. As part of a study on thermal analysis of solids, thermal decomposition studies of some complexes of lanthanide (III) ions with NTA (nitrile triacetic acid) have been carried out using simultaneous thermogravimetry (TG), derivative thermogravimetry (DTG) and differential thermal analysis (DTA) techniques. The results of these studies are presented in this paper.

EXPERIMENTAL

Complexes of nine lanthanides with NTA were prepared 1. The nine lanthanides chosen were La, Pr, Nd, Sm, Eu, Gd, Tb, Dy and Yb. Lanthanide (III) carbonate (0.5 g;1.15 mmol) and complexone (H3 NTA : 0.45g ;2.3 mmol) were taken in RB flask, and 50 ml of water was added to it. The reaction mixture was shaken vigorously so that the complex was formed with the evolution of carbon dioxide. When the reaction was complete, a clear solution was obtained and the evolution of carbon dioxide ceased. The solution was evaporated to dryness on a boiling water bath to get the solid complex, which was dried in vacuo over phosphorus (V) oxide.

The TG, DTG and DTA curves of the complexes were recorded on a Mettler Toledo thermal analysis system in air and in nitrogen with a heating rate of 100 C min-1 and a sample mass of ~ 3 mg in the temperature range 30-8000C.The curves thus obtained were exactly traced present them in the thesis. The ultimate decomposition product in each stage was obtained by independent pyrolysis experiment, and it was characterized by chemical analysis. The kinetics and mechanisms of thermal decomposition reactions were elucidated using the Coats Redfern equation 2 and the mechanistic equations proposed by Satava3.

RESULTS AND DISCUSSIONS

Phenomenological Aspects of Thermal Decomposition Studies:

The phenomenological aspect of the thermal behavior of NTA complexes of lanthanide in air as well as nitrogen is discussed below.

[La (NTA)].3 H_2O :

The complex is stable upto ~1100 C in air. Then it undergoes decomposition in three stages as shown by the DTG peaks at 160,405 and 6760C, and the corresponding DTA peaks at 158,394 and 676^0C. The first

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decomposition stage corresponds to the dehydration of the complex with the removal of all the water molecules present in it. The mass loss data obtained from the TG curve (13.7%) and the calculated value (14.0%) for the first decomposition stage support the removal of 3 water molecules. The second stage is the major decomposition stage of the complex, and the exothermicity of the DTA peak for this stage suggests the oxidative decomposition of the complex. The third stage is a minor decomposition stage, in which the carbonaceous matter is eliminated to give La_2O_3 as the final residue after ~ 700^0C, which was identified by chemical analysis. The total mass loss data obtained from the TG curve (62.2%), independent pyrolysis experiment (60.2%) and the calculated value (57.6%) support the above suggested decomposition reaction. The complex is stable upto ~ 130^0C and it undergoes decomposition in two stages in nitrogen atmosphere. The DTG peaks corresponding to these decomposition stages are observed at 156 and 403^0C, and the corresponding DTA peaks at 158 and 403^0C. The first stage is the dehydration step, which involves the removal of three water molecules. The mass loss data obtained from the TG curve (11.6%) and the calculated value (14.0%) support the presence of three water molecules in the complex. The second stage corresponds to the decomposition of the anhydrous complex to give La_2O_3 as the residue after @ 740^0C. The DTA peak corresponding to this decomposition stage is exothermic in nature, probably due to partial oxidation of the carbonaceous matter using the oxygen present in the molecule. The residue obtained after ~ 740^0C was identified by chemical analysis. Mass loss data obtained from the TG curve (61.6%), pyrolysis experiment (59.8%) and the calculated value (57.6%) agree the above suggested decomposition reaction.

[Nd (NTA)].$3H_2O$:

This complex is stable upto ~ 2200C in air, and it decomposes in two stages as shown by the DTG peaks at 405 and 470^0C, and the corresponding DTA peaks at 405 and 469^0C. The first decomposition stage corresponds to dehydration and partial decomposition of the complex with the removal of all the three water molecules present in it. The second stage is the major decomposition of the complex, and exothermicity of the DTA peak for this stage suggests the oxidative decomposition of the complex. The final residue obtained after ~ 700^0C was found to be Nd_2O_3 which was identified by chemical analysis. The total mass loss data obtained from the TG curve (50.8%), independent pyrolysis (52.7%) and the calculated value (54.7%) support the above suggested decomposition reaction. The complex is stable upto ~ 240^0C, and it undergoes decomposition in a single stage in nitrogen atmosphere. The DTG peak corresponding to this decomposition stage is observed at 404^0C, and the corresponding endothermic peak at 400^0C.Here the dehydration and decomposition takes place simultaneously in a single stage with the formation of Nd_2O_3 as the decomposition residue after ~ 800^0C.The mass loss data obtained from TG curve (52.2%), pyrolysis experiment (51.9%) and the calculated value (54.7%) agree with the above suggested decomposition reaction.

[Sm (NTA)].$3H_2O$:

The Sm complex is stable upto ~ 220^0C in air. Then it undergoes decomposition in two stages as shown by the DTG peaks at 404 and 468^0C, and the corresponding DTA peaks at 406 and 466^0C. The first stage involves dehydration and partial decomposition of the complex, and the decomposition is completed in the second stage with the formation of Sm_2O_3 as the residue after ~ 650^0C.The extent of decomposition of the complex in the second stage is not known with certainty as there is no stability region in between the two decomposition stages. The final residue is found to be Sm_2O_3 by chemical analysis, the suggested decomposition reaction is supported by the mass loss data obtained from the TG curve (53.7%) , pyrolysis experiment (55.2%) and the calculated value (56.8%) The complex is stable upto ~ 350^0C, and it decomposes in a single stage in nitrogen as denoted by the DTG peak at 404^0C, and the corresponding exothermic DTA peak at 404^0C.The decomposition is continued upto ~ 700^0C with gradual mass loss, which is attributed to the removal of carbonaceous matter obtained in the decomposition reaction. The decomposition of the complex corresponds to the simultaneous dehydration of three water molecules and the decomposition of NTA molecule. The total mass loss obtained after ~ 700^0C from the TG curve (64.4%), pyrolysis experiment (62.3%) and the calculated value (56.8%) agree well for the suggested decomposition reaction to form Sm2O3 as the final decomposition residue as confirmed by chemical analysis. [Eu(NTA)].$6H_2O$

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The Eu complex is stable upto ~ 100^0C in air. Then it undergoes decomposition in two stages as shown by the DTG peaks at 160, and 362^0C and the 6 corresponding DTA peaks at 162 and357^0C. The first decomposition stage corresponds to the removal of two of the six water molecules present in it. The mass loss data obtained from the TG curve (6.8%) and the calculated value (7.9%) for the first decomposition stage support the removal of two water molecules. The second stage is the major decomposition stage of the complex, in which the remaining four water molecules are removed along with the decomposition of the complex to give Eu_2O_3 as the final residue after @ 700^0C.The total mass loss data obtained from the TG curve (65.3%), independent pyrolysis (60.2%) and the calculated value (57.7%) support the above suggested decomposition reaction. The complex is stable upto ~ 100^0C, and it undergoes decomposition in two stages in nitrogen atmosphere. The DTG peaks corresponding to these decomposition stages are observed at 156 and 384^0C and the DTA peaks at 158 and 370^0C.The first stage is the dehydration step, which involves the removal of two water molecules. The mass loss data obtained from the TG curve (7.2%) and the calculated value (7.9%) support the removal of two water molecules. The second stage is the major decomposition of the complex, and exothermicity of the DTA peak for this stage suggests the oxidative decomposition of the complex, in which the carbonaceous matter is eliminated to give Eu_2O_3 as the final residue after @ 750^0C, which is identified by chemical analysis. The total mass loss data obtained from the TG curve (62.9%), independent pyrolysis (60.2%) and the calculated value (57.7%) support the above suggested decomposition reaction.

[Gd (NTA).].$6H_2O$:

The complex is stable upto ~ 340^0C in air. It decomposes in a single stage in air, and this decomposition is denoted by the DTG peak at 403^0C and the corresponding exothermic DTA peak at 404^0C.The decomposition is continued upto ~ 700^0C with 7 gradual mass loss, which is attributed to the removal of carbonaceous matter obtained in the decomposition reaction. The decomposition of the complex corresponds to simultaneous decomposition of NTA molecule present in the complex. The total mass loss obtained after @ 700^0C from the TG curve (66.4%), pyrolysis experiment (64.6%) and the calculated value (60.3%) agree well for the suggested decomposition reaction to form Gd_2O_3 as the final decomposition residue, which was confirmed by chemical analysis. The complex is stable upto ~ 360^0C in nitrogen also. It decomposes in a single stage in nitrogen as well, and this decomposition stage is denoted by the DTG peak at 403^0C and the corresponding endothermic peak at 400^0C.The decomposition s continued upto ~ 800^0C with gradual mass loss, which is attributed to the removal of carbonaceous matter obtained in the decomposition reaction. The decomposition of the complex corresponds to simultaneous dehydration of six water molecules and the decomposition of EDTA molecule present in the complex. The total mass loss obtained after ~ 800^0C from the TG curve (60.8%) , pyrolysis experiment (60.3%) and the calculated value (60.3%) agree well for the suggested decomposition reaction to form Gd2O3 as the final decomposition residue ,which is confirmed by chemical analysis.

[Tb(NTA)].$6H_2O$

The complex of Tb with NTA is stable upto ~ 100^0C in air. It undergoes decomposition in two stages as indicated by the DTG peaks at 156 and 399^0C, and the corresponding DTA peaks at 158 and 400^0C. The first decomposition stage corresponds to the loss of six water molecules. Mass loss data obtained from TG (19.8%) and calculated value (23.5%) are in reasonable agreement. The second stage is the remaining decomposition of the complex to give Tb2O3 as the final residue after ~ 6000C. The mass loss data obtained from the TG curve (64.9%), pyrolysis experiment (62.0%) and the calculated value (60.1%) support the suggested decomposition. The complex is stable upto ~ 130^0C in nitrogen. Then it undergoes decomposition in two stages as shown by the DTG peaks at 152 and 411 and the corresponding DTA peaks at 155 and 400^0C.The first decomposition stage corresponds to the removal of two of the six water molecules present in it. The mass loss data obtained from the TG curve (9.0%) and the calculated value (7.8%) for the first decomposition stage support the removal of two water molecules. The second stage is the major decomposition stage of the complex , in which the remaining four water molecules are removed along with the decomposition of the complex to give Tb_2O_3 as the final residue after ~ 800^0C.The total mass loss data obtained from the TG curve (51.3%) ,independent pyrolysis (54.8%) and the calculated value (56.7%) support the above suggested decomposition

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reaction. 8.[Dy (NTA)].6H_2O The Dy complex is stable upto ~ 220^{0}C in air and it undergoes decomposition in two stages as denoted by the DTG peaks at 403 and 477^{0}C and the corresponding exothermic DTA peaks at 404 and 475^{0}C. The first decomposition stage involves the dehydration and partial decomposition of the complex, and the decomposition is completed in the second stage with the formation of Dy_2O_3 as the residue after ~ 700^{0}C.The extent of decomposition of the complex in the first stage is not known with certainty as there is no stability region in between the two decomposition stages. The final residue is found to be Dy_2O_3 by chemical analysis, and the suggested decomposition reaction is supported by mass loss data obtained from the TG curve (57.6%) , pyrolysis experiment (56.2%) and the calculated value (59.6%). The complex is stable upto ~ 320^{0}C, in nitrogen, and it undergoes decomposition in a single stage as denoted by the exact parallel DTG peak and the 9 exothermic DTA peak both observed at 400^{0}C.The decomposition is completed to giveDy_2O_3 as the residue after ~ 750^{0}C.The residue obtained after ~ 7500C is identified by chemical analysis. Mass loss data obtained from the TG curve (60.5%), pyrolysis experiment (59.2%) and the calculated value (59.6%) agree well with the above suggested decomposition reaction.

[Yb(NTA)].6H_2O:

The complex of Yb with NTA is stable upto ~ 80^{0}C in air. It undergoes decomposition in two stages as indicated by the DTG peaks at 115 and 419^{0}C and the corresponding DTA peaks at 118 and 419^{0}C. The first decomposition stage corresponds to the loss of two water molecules. Mass loss data obtained from the TG curve (9.6%) and the calculated value (7.6%) agree with the removal of two water molecules. The second stage is the major decomposition stage of the complex, in which the remaining four water molecules are removed along with the decomposition of the complex to give Yb_2O_3 as the final residue after~ 600^{0}C.The mass loss data obtained from the TG curve (60.6%), pyrolysis experiment (58.0%) and the calculated value (54.9%) support the above suggested decomposition. The complex is stable upto @ 100^{0}C in nitrogen atmosphere, and it decomposes in two stages as indicated by the DTG peaks at 113 and 416^{0}C, and the corresponding endothermic peaks at 113 and 416^{0}C and the corresponding endothermic peaks at 117 and 419^{0}C. In the first stage two of the six water molecules are eliminated, which is supported by the mass loss obtained from the TG curve (7.5%) and the calculated value (7.6%). In the second stage, the remaining four water molecules are lost along with the decomposition of the complex. The residue obtained after ~ 800^{0}C is found to be Yb_2O_3 by chemical analysis ,which is in conformity with the mass loss data obtained from the TG curve (53.1%),pyrolysis experiment (54.2%),and the calculated 10 value.(54.9%) Among the nine NTA complexes of lanthanides studied, the complexes of the early members of lanthanides, viz, those of La, Pr, Nd and Sm have three water molecules each, while the complexes of latter lanthanides, viz, those of Eu, Gd, Tb, Dy and Yb have six water molecules. These complexes are stable at least upto ~100^{0}C.The dehydration and decomposition occur simultaneously in almost all complexes. Dehydration occurs in two stages in the complexes of Eu, Tb, and Yb with the removal of two water molecules in the first stage and the remaining four in the second stage along with the decomposition in nitrogen atmosphere. More decomposition stages are observed in air than in nitrogen in all the complexes. The stabilities of the complexes are greater in nitrogen than in air. However, the final residues obtained in both the atmospheres are the stable oxides, Ln2O3 for all but that of Pr, for which Pr6O11 is obtained as the final residue. The decomposition reactions are completed with the formation of the lanthanide oxides at a lower temperature in air than in nitrogen. The stability order of the complexes in air and in nitrogen are given below on the basis ofthe first DTG peak temperatures of the complexes as given in parenthesis.

In air: [Yb(NTA)].6H 2 O < [Tb(NTA)].6H 2 O < [Eu(NTA)].6H 2 O = [La (NTA)].3H 2 O < (115 0 C) (156 0 C) (160 0 C) (160 0 C) Dy(NTA).6H 2 O= Gd(NTA).6H 2 O= [Pr(NTA)].3H 2 O< [Sm(NTA)].3H 2 O< (403 0 C) (403 0 C) (403 0 C) (404 0 C) [Nd(NTA)].3H 2 O (405 0 C) In nitrogen: [Yb(NTA)].6H 2 O < [Tb(NTA)].6H 2 O < Eu(NTA).6H 2 O = [La (NTA)].3H 2 O < (113 0 C) (152 0 C) (156 0 C) (156 0 C) [Dy(NTA)].6H 2 O] < [Py(NTA)].3H 2 O]<[Gd(NTA)].6H 2 O <[Nd(NTA)].3H 2 O (400 0 C) (402 0 C) (403 0 C) (404 0 C) =[Sm(NTA)].3H 2 O (404 0 C)

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Tables 3 and 4 tabulates Kinetic parameters of Lanthanide (III) complexes with NTA in air and in Nitrogen respectively using Coats-Redfern equation.

Table 3. Kinetic parameters of Lanthanide (III) complexes with NTA in air using Coats-Redfern equation

Complex	Decomposition stage	Ts		Order parameter 'n'	Activation energy ,E (kJ/mol)	Pre-exponential factor, A (s^{-1})	Energy of Activation,ΔS (J/K/mol)	Correlation Coefficient 'r'
		^{0}C	K					
La(NTA).3H_2O	I	160	433	1.0	69.4	3.00 x 10^4	-181.4	0.9580
	II	405	678	0.6	280.8	6.09 x 10^{22}	184.5	0.9967
	III	676	949	0.9	584.8	2.11 x 10^{23}	383.4	0.9987
Pr (NTA).3H_2O	I	403	676	0.9	754.9	4.36 x 10^{59}	890.0	0.9999
	II	497	770	1.6	328.5	6.59 x 10^{23}	203.2	0.9987
Nd(NTA).3H_2O	I	405	678	1.7	538.5	2.88 x 10^{42}	561.1	0.9997
	II	470	743	0.7	133.6	1.65 x 10^{10}	-56.8	0.9964
Sm(NTA).3H_2O	I	404	677	1.8	853.0	1.01 x 10^{67}	1030.9	0.9998
	II	468	741	0.6	83.2	2.36 x 10^6	-130.4	0.9999
Eu(NTA).6H_2O	I	160	433	1.0	55.7	24.90	-221.2	0.9768
	II	362	635	1.5	300.2	7.10 x 10^{25}	243.7	0.9957
Gd (NTA).6H_2O	I	403	676	1.8	387.1	7.64 x 10^{30}	339.5	0.9945
Tb(NTA).6H_2O	I	156	429	1.0	48.2	1.94	-242.4	0.9844
	II	399	672	1.7	324.7	2.77 x 10^{26}	254.6	0.9982
Dy (NTA).6H_2O	I	403	676	0.7	388.3	1.05 x 10^{11}	-40.7	0.9997
	II	477	750	1.3	197.4	6.09 x 10^{14}	30.5	0.9955
Yb(NTA).6H_2O	I	115	388	1.0	59.6	467.5	-195.8	0.9876
	II	419	692	0.5	509.9	4.38 x 10^{39}	506.9	0.9915

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Table 4. Kinetic parameters of Lanthanide (III) complexes with NTA in nitrogen using Coats-Redfern equation

Complex	Decomposition stage	Ts		Order parameter 'n'	Activation energy ,E (kJ/mol)	Pre-exponential factor, A	Energy of Activation,ΔS (J/K/mol)	Correlation Coefficient 'r'
		^{0}C	K					
La(NTA).3H$_2$O	I II III	156 403	429 676	1.0 2.6	111.2 570.5	7.77x 10^7 4.05x 10^{45}	-96.9 621.4	0.9968 0.9985
Pr (NTA).3H$_2$O	I	402	675	2.3	377.5	3.21x 10^{30}	331.9	0.9990
Nd(NTA).3H$_2$O	I	404	677	1.9	645.5	4.76x 10^{50}	718.4	0.9874
Sm(NTA).3H$_2$O	I	404	677	0.7	81.8	6.95x 10^6	-120.7	0.9997
Eu(NTA).6H$_2$O	I II	156 384	429 657	1.0 1.1	104.1 196.7	2.49x 10^7 3.84x10^{16}	-106.3 66.0	0.9788 0.9928
Gd (NTA).6H$_2$O	I	403	676	1.5	236.9	2.47x 10^{19}	119.5	0.9998
Tb(NTA).6H$_2$O	I II	152 411	425 684	1.0 1.2	126.7 362.4	2.38x 10^{10} 5.08x10^{28}	-49.2 297.7	0.9592 0.9695
Dy (NTA).6H$_2$O	I	400	673	0.8	113.8	2.95x 10^9	-70.3	0.9998
Yb(NTA).6H$_2$O	I II	113 416	386 689	1.0 1.1	82.9 192.8	1.15x 10^6 2.09x10^{15}	-128.3 41.5	0.9832 0.9881

Table 5 and 6 tabulates Kinetic parameters of lanthanide (III) complexes with NTA in air and in nitrogen respectively using mechanism based equation

Table 5 Kinetic parameters of lanthanide (III) complexes with NTA in air using mechanism based equation

Complex	Decomposition stage	Ts		Mechanism followed	Activation energy ,E	Pre-exponenti	Energy	Correlation
		^{0}C	K					

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					(kJ/mol)	al factor, A (s^{-1})	of Activation, ΔS (J/K/mol)	Coefficient 'r'
La(NTA).3H_2O	I	160	433	Random Nucleation	69.4	3.00×10^{4}	-181.4	0.9968
	II	405	678	Random Nucleation	271.7	5.34×10^{22}	183.4	0.9967
	III	676	949	Random Nucleation	597.4	1.11×10^{33}	378.1	0.9986
Pr (NTA).3H_2O	I	403	676	Random Nucleation	712.5	5.25×10^{59}	891.5	0.9989
	II	497	770	Random Nucleation	286.5	5.46×10^{23}	201.6	0.9999
Nd(NTA).3H_2O	I	405	678	Random Nucleation	646.7	8.04×10^{44}	494.5	0.9899
	II	470	743	Random Nucleation	151.5	4.25×10^{5}	-144.7	0.9955
Sm(NTA).3H_2O	I	404	677	Random	897.50	7.60×10^{67}	1047.7	0.9710
	I	468	741	Nucleation	74.50	9.36×10^{6}	-119.0	0.9998
	I			Random Nucleation				
Eu(NTA).6H_2O	I	160	433	Random Nucleation	55.7	24.90	-221.2	0.9990
	II	362	635	Random Nucleation	236.6	2.49×10^{25}	234.9	
Gd (NTA).6H_2O	I	403	676	Random Nucleation	378.3	1.61×10^{30}	326.5	0.9899

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NTA).6H_2O	I I I	156 399	429 672	Random Nucleation Random Nucleation	48.2 269.86	1.94 8.58x 10^{15}	-242.4 53.4	0.9844 0.9959
Dy (NTA).6H_2O	I II	403 477	676 750	Random Nucleation Random Nucleation	297.2 173	1.06x 10^{11} 6.63x10^{14}	-40.6 31.2	0.9999 0.9934
Yb(NTA).6 H_2O	I II	115 419	388 692	Random Nucleation Random Nucleation	59.6 483.2	467.50 3.7x10^{39}	-195.8 505.5	0.9876 0.9864

Table 6 Kinetic parameters of lanthanide (III) complexes with NTA in nitrogen using mechanism based equation

Complex	Decomposition stage	Ts		Mechanism followed	Activation energy ,E (kJ/mol)	Pre-exponential factor, A (s^{-1})	Energy of Activation, ΔS (J/K/mol)	Correlation Coefficient 'r'
		^{0}C	K					
La(NTA).3H_2O	I I I	156 403	429 676	Random Nucleation Random Nucleation	111.2 570.0	7.77x10^7 4.75x10^7	-96.9 622.2	0.9968 0.9849
Pr (NTA).3H_2O	I	402	675	Random Nucleation	385.4	1.01x10^7	322.6	0.9544

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Nd(NTA).3H$_2$O	I	404	677	Random Nucleation	539.8	2.10x10^7	635.0	0.9822
Sm(NTA).3 H$_2$O	I	404	677	Random Nucleation	80.6	5.46x10^7	-122.7	0.9710
Eu(NTA).6H$_2$O	I I I	156 384	429 657	Random N ucleation Random Nucleation	104.1 186.5	2.49x10^7 5.17x10^7	-106.3 68.5	0.9788 0.9926
Gd (NTA).6H$_2$O	I	403	676	Random Nucleation	270.2	2.48x10^7	119.5	0.9603

Tb(NTA).6H$_2$O	I II	152 411	425 684	Random Nucleation Random Nucleation	126.7 330.9	2.38x10^7 1.63x10^7	-49.2 288.2	0.9592 0.9687
Dy (NTA).6H$_2$O	I	400	673	Random Nucleation	148.6	3.29x10^7	-69.5	0.9916
Yb(NTA).6H$_2$O	I II	113 416	386 689	Random Nucleation Random Nucleation	82.9 177.3	1.15x10^7 1.28x10^7	-128.3 37.3	0.9832 0.988

Kinetics and mechanism of thermal decomposition reactions The kinetics and mechanism of thermal decomposition reactions of the nine NTA complexes of lanthanides have been studied using respectively , the Coats Redfern equation and the mechanistic equations proposed by Satava. The kinetic parameters calculated using the Coats Redfern equation for the decomposition of NTA complexes of lanthanides in air and in nitrogen are given in tables 3 and 4.The La complex decomposes in three stages, while the Pr, Nd, Sm, Eu, Tb, Dy and Yb complexes decompose in two stages and the Gd complex in a single stage in air. In nitrogen, the La, Eu, Tb, and Yb complexes decompose in two stages while the Pr, Nd, Sm, Gd and Dy complexes undergo single stage decomposition. The salient features of the kinetics and mechanism of these NTA complexes are discussed below. The values of the order parameter for the decomposition of the nine NTA complexes of lanthanides are in the range 0.5-1.8, while they are in the range of 0.7-2.6 in nitrogen. The values of activation energies are in the range 48.2-853.0 kJ/mol in air and these values are in the range 81.8 to 645.5 kj/ mol in nitrogen. The highest value of activation energy is observed for the first decomposition stage of the

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samarium complex in air and the lowest value for the dehydration stage of the Terbium complex in air. The values of pre exponential factor are in the range 1.94-1.01x10 67 s-1, the lowest value being for first stage decomposition of the terbium complex in air, and the highest value for the first stage decomposition of the samarium complex in air. The values of entropy of activation are directly related to the values of pre exponential factor. Positive values of entropy of activation are obtained for most of the decomposition stages studied. A positive value of entropy of activation indicates that the activated complex is less ordered than the reactants, while a negative value for the entropy of activation indicates that the activated complex is more ordered than the reactants. All the decomposition stages of the nine complexes of lanthanides with NTA follow the Mampel equation in air as well as in nitrogen, suggesting that the rate controlling process is random nucleation with the formation of one nucleus on each particle. The kinetic parameters calculated using the mechanistic equation are comparable with those obtained by the Coats Redfern equation in all the cases. Therefore, the proposed mechanism for the thermal decomposition reactions of these complexes is acceptable.

Summary and Conclusion :

Among the nine NTA complexes of lanthanides studied, the complexes of the early members of the lanthanides,viz.,those of La, Pr, Nd, and Sm have three water molecules each ,while the complexes of latter lanthanides ,viz., those of Eu, Gd, Tb, Dy and Yb have six water molecules. These complexes are stable atleast upto ~100 0 C.The dehydration and decomposition occur simultaneously in almost all the complexes. Dehydration occurs in two stages in the complexes of Eu, Tb and Yb with the removal of two water molecules in the first stage and the remaining four in the second stage along with the decomposition in nitrogen atmosphere. More decomposition stages are observed in air than in nitrogen in all the complexes. The stabilities of the complexes are greater in nitrogen than in air. However ,the final residues obtained in both the atmospheres are the stable oxides, Ln 2 O 3 for all except that of Pr, for which Pr 6 O 11 is obtained as the final residue. The decomposition reactions are completed with the formation of the lanthanide oxides at a lower temperature in air than in nitrogen.

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