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Thermal Decomposition Studies of Lanthanide(III) Complexes of Diethylenetriaminepentaacetic Acid

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Thermal decomposition studies of lanthanide(III) complexes of diethylenetriaminepentaacetic acid (DTPA) in air is studied using simultaneous TG-DTA. Nine lanthanides chosen are La, Pr, Nd, Sm, Eu, Gd, Tb, Dy and Yb. The phenomenological as well as the kinetic aspects of thermal decomposition is described. Kinetic parameters are calculated. The stability of the complexes in air is assessed.

Key Words: Lanthanide(III), Diethylenetriaminepentaacetic acid, Phenomenological, Kinetic, TG, DTA.

INTRODUCTION

In recent times, increasing interest has been developed on the thermal decomposition studies including the kinetics and mechanism of metal complexes. Both the isothermal and non-isothermal methods have been used for the evaluation of kinetic parameters and for the elucidation of the mechanisms of thermal decomposition reactions. In present studies, the thermal decomposition studies of some diethylenetriaminepentaacetic acid (DTPA) complexes of lanthanides using simultaneous TG-DTA techniques in two distinct atmospheres, *viz.*, air and nitrogen are discussed.

EXPERIMENTAL

All the lanthanide(III) complexones used for the present investigation were prepared as described previously[1]. Lanthanide carbonate, (0.5 g; 1.15 mmol) and complexone (H_5DTPA: 0.9 g; 3.3 mol) were taken in an round bottom flask and 50 mL water was added in 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 filtered to remove any unreacted reagents, if any. This solution was evaporated to dryness on a boiling water bath to get the solid complex, which was dried *in vacuo* over phosphorus(V) oxide.

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Complexes of La(III), Pr(III), Nd(III), Sm(III), Eu(III), Gd(III), Tb(III), Dy(III) and Yb(III) with DTPA were prepared and characterized. The TG, DTG and DTA curves of all the complexes were recorded on a Mettler Toledo TGA/SDTA 851e thermal analysis system in air atmosphere in the temperature region 30-800 ºC. The plateau in the TG curves, the peak temperatures and the peak widths in the DTG and DTA curves were tabulated. The kinetic parameters such as order parameter (n), energy of activation (E), pre-exponential factor (A) and entropy of activation (ΔS) were calculated for all the well-defined major decomposition stages using the Coats-Redfern[2] equation. The mechanisms of the thermal decomposition reactions were elucidated for various thermal decomposition stages of the complexes using the mechanistic equations proposed by Satava[3]. A heating rate of 10 ºC/min and a sample mass of *ca.* 3 mg have been used throughout the measurement.

RESULTS AND DISCUSSION

Among the nine DTPA complexes of the lanthanides studied, all the complexes have only one water molecule each. These complexes are stable at least upto *ca.* 200 ºC indicating that the water molecules are strongly coordinated to the lanthanide ions. Moreover, the dehydration and the decomposition of the complexes occur in distinct stages in all the complexes. The final residue obtained in each of the complexes is the stable oxide, Ln_2O_3, except that of Pr, for which the higher oxide, Pr_6O_{11} is formed. All the complexes undergo exothermic reactions in air. The exothermicity of the decomposition reactions in air is attributed to oxidative decomposition. The decomposition reactions complete at a temperature 520-640 ºC. The stability orders of the complexes in air (on the basis of the DTG peak temperature of the first decomposition stage as given in parenthesis).

In air: $H_2[Tb(DTPA)]\cdot H_2O < H_2[Eu(DTPA)]\cdot H_2O = H_2[Dy(DTPA)]\cdot H_2O < H_2[Nd(DTPA)]\cdot H_2O < H_2[Gd(DTPA)]\cdot H_2O = H_2[Yb(DTPA)]\cdot H_2O < H_2[Sm(DTPA)]\cdot H_2O < H_2[Pr(DTPA)]\cdot H_2O < H_2[La(DTPA)]\cdot H_2O$.

Kinetics and mechanism of thermal decomposition reactions

The kinetics and mechanism of thermal decomposition reactions of all the nine DTPA complexes of lanthanides have been studied using the Coats-Redfern equation[2] and the mechanistic equations proposed by Satava[3]. The kinetic parameters calculated using the Coats-Redfern equation for the decomposition of these complexes in air is given in Table-2. All the complexes decompose in three stages in air. The salient features of the kinetics and mechanism of DTPA complexes in air are discussed below.

The values of the order parameter for the decomposition of the nine DTPA complexes of lanthanides in air are in the range 0.5-2.5. The values of activation energy are in the range 56.2-543.7 kJ mol^{-1} in air. The highest value of activation energy is observed for the second decomposition stage

TABLE-1
THERMAL DECOMPOSITION DATA OF LANTHANIDE(III) COMPLEXES WITH DTPA IN AIR

Complex	Plateaus in TG (ºC)	Decomp. stages	Peak temp. in DTG (ºC)	Peak Widths in DTG (ºC)	Peak temp in DTA (ºC)	Peak width in DTA (ºC)	Mass loss (%)		Residue
							From TG	Calculated	
$H_2[La(DTPA)].H_2O$	Upto200	I	257	240-280	266 (endo)	230-280	3.1	3.2	$H_2[La(DTPA]$
	280-340	II	373	360-400	377 (exo)	340-400	28.0	–	–
	After 640	III	508	460-520	505 (exo)	460-520	65.0	70.5	La_2O_3
$H_2[Pr(DTPA)].H_2O$	Upto200	I	253	240-280	250 (endo)	210-260	3.2	3.1	$H_2[Pr(DTPA]$
	260-340	II	375	360-400	369 (exo)	360-380	30.4	–	–
	After 540	III	525	500-560	525 (exo)	500-560	67.8	69.3	Pr_6O_{11}
$H_2[Nd(DTPA)].H_2O$	Upto200	I	243	220-280	260 (endo)	220-270	4.2	3.2	$H_2[Nd(DTPA)]$
	270-320	II	378	360-400	378 (exo)	370-390	37.4	–	–
	After 600	III	515	480-520	515 (exo)	480-520	72.7	69.8	Nd_2O_3
$H_2[Sm(DTPA)].H_2O$	Upto220	I	248	220-260	250 (endo)	210-260	3.8	3.2	$H_2[Sm(DTPA)]$
	270-340	II	381	320-400	384 (exo)	370-400	35.8	–	–
	After 600	III	519	460-520	521 (exo)	480-540	66.4	69.1	Sm_2O_3
$H_2[Eu(DTPA)].H_2O$	Upto220	I	241	220-280	243 (endo)	230-260	3.8	3.2	$H_2[Eu(DTPA]$
	300-360	II	384	360-400	389 (exo)	370-400	46.1	–	–
	After 550	III	442	420-482	445 (exo)	420-450	68.6	68.9	Eu_2O_3
$H_2[Gd(DTPA)]H_2O$	Upto200	I	246	220-280	245 (endo)	220-260	3.4	3.2	$H_2[Gd(DTPA)]$
	280-360	II	382	360-400	381 (exo)	370-390	21.7	–	–
	After 540	III	526	500-560	525 (exo)	500-540	64.1	68.3	Gd_2O_3
$H_2[Tb(DTPA)]H_2O$	Upto200	I	239	220-280	240 (endo)	220-250	2.9	3.1	$H_2[Tb(DTPA]$
	260-300	II	385	380-400	388 (exo)	370-400	37.9	–	–
	After 540	III	513	480-520	505 (exo)	480-520	65.4	68.0	Tb_2O_3
$H_2[Dy(DTPA)].H_2O$	Upto220	I	241	220-280	240 (endo)	220-250	2.9	3.2	$H_2[Dy(DTPA)]$
	260-340	II	386	360-400	389 (exo)	370-400	34.7	–	–
	After 540	III	525	480-530	525 (exo)	490-530	65.1	66.6	Dy_2O_3
$H_2[Yb(DTPA)].H_2O$	Upto200	I	246	220-260	247 (endo)	220-260	2.2	3.1	$H_2[Yb(DTPA)]$
	300-360	II	398	380-400	394 (exo)	370-400	36.7	–	–
	After 520	III	480	460-520	481 (exo)	460-500	62.0	66.4	Yb_2O_3

TABLE-2

KINETIC PARAMETERS OF LANTHANIDE(III) COMPLEXES WITH DTPA IN AIR USING COATS-REDFERN EQUATION

Complex	Decomp. stage	Temp. (ºC)	Order parameter 'n'	Activation energy (E) (kJ mol^{-1})	Pre-exponential factor (A) (s^{-1})	Entropy of activation (ΔS) (JK^{-1} mol^{-1})	Correlation coefficient (r)
$H_2[La(DTPA)].H_2O$	I	257	1.0	237.0	8.31×10^{18}	112.50	0.9930
	II	373	0.5	56.2	1.02×10^{5}	-155.40	0.9899
	III	508	0.8	81.8	4.93×10^{5}	-143.90	0.9732
$H_2[Pr(DTPA)].H_2O$	I	253	1.0	238.0	1.10×10^{19}	114.60	0.9931
	II	375	1.8	424.8	6.15×10^{35}	433.70	0.9731
	III	525	2.5	206.2	8.32×10^{15}	51.70	0.9891
$H_2[Nd(DTPA)]H_2O$	I	243	1.0	153.2	3.34×10^{10}	-47.90	0.9962
	II	378	1.1	188.0	1.21×10^{16}	56.50	0.9863
	III	515	0.8	77.8	2.60×10^{5}	-147.70	0.9954
$H_2[Sm(DTPA)]H_2O$	I	248	1.0	237.2	1.10×10^{19}	114.90	0.9954
	II	381	0.5	239.9	1.13×10^{20}	132.50	0.9833
	III	519	1.3	143.3	6.32×10^{10}	-46.20	0.9917
$H_2[Eu(DTPA)].H_2O$	I	241	1.0	173.1	3.83×10^{12}	-8.52	0.9890
	II	384	0.8	543.7	2.81×10^{44}	599.40	0.9933
	III	442	1.1	247.0	5.95×10^{18}	107.20	0.9768
$H_2[Gd(DTPA)].H_2O$	I	246	1.0	176.2	6.00×10^{12}	-4.90	0.9967
	II	382	0.9	222.8	2.65×10^{18}	101.30	0.9835
	III	526	1.3	91.8	8.08×10^{6}	-120.80	0.9761
$H_2[Tb(DTPA)].H_2O$	I	239	1.0	150.8	3.60×10^{10}	-47.30	0.9965
	II	385	0.6	433.0	3.76×10^{35}	429.60	0.9993
	III	513	0.8	118.8	6.45×10^{8}	-84.30	0.9979
$H_2[Dy(DTPA)].H_2O$	I	241	1.0	190.3	1.91×10^{14}	23.90	0.9920
	II	386	0.5	280.5	1.98×10^{23}	194.50	0.9965
	III	525	1.7	146.7	$1.61 x10^{10}$	-57.70	0.9992
$H_2[Yb(DTPA)].H_2O$	I	246	1.0	215.5	8.02×10^{16}	74.10	0.9939
	II	398	0.8	373.5	1.36×10^{30}	325.30	0.9969
	III	480	0.9	106.1	1.18×10^{8}	-98.00	0.9993

TABLE-3

KINETIC PARAMETERS OF LANTHANIDE(III) COMPLEXES WITH DTPA IN AIR USING MECHANISM BASED EQUATION

Complex	Decomposition stage	Temp. (ºC)	Mechanism followed	Activation energy (E) (kJ mol^{-1})	Pre-exponential factor (A) (s^{-1})	Entropy of activation (ΔS) (JK^{-1} mol^{-1})	Correlation coefficient (r)
$H_2[La(DTPA)].H_2O$	I	257	Random nucleation	235.0	8.51×10^{18}	112.70	0.9899
	II	373	Random nucleation	55.8	1.00×10^{5}	-155.60	0.9822
	III	508	Random nucleation	80.7	4.87×10^{5}	-144.00	0.9904
$H_2[Pr(DTPA)].H_2O$	I	253	Random nucleation	239.5	1.23×10^{19}	115.80	0.9951
	II	375	Random nucleation	420.5	6.58×10^{35}	434.30	0.9642
	III	525	Random nucleation	204.8	8.30×10^{15}	499.70	0.9659
$H_2[Nd(DTPA)].H_2O$	I	243	Random nucleation	150.2	2.98×10^{10}	-489.20	0.9866
	II	378	Random nucleation	186.5	1.19×10^{16}	56.40	0.9863
	III	515	Random nucleation	75.7	2.50×10^{5}	-149.60	0.9911
$H_2[Sm(DTPA)].H_2O$	I	248	Random nucleation	230.6	1.20×10^{19}	115.70	0.9954
	II	381	Random nucleation	239.8	1.00×10^{20}	131.40	0.9852
	III	519	Random nucleation	140.1	6.51×10^{10}	-46.00	0.9865
$H_2[Eu(DTPA)].H_2O$	I	241	Random nucleation	170.5	3.98×10^{12}	-8.22	0.9964
	II	384	Random nucleation	548.6	2.75×10^{44}	599.20	0.9930
	III	442	Random nucleation	247.5	6.00×10^{18}	107.30	0.9932
$H_2[Gd(DTPA)].H_2O$	I	246	Random nucleation	179.1	5.10×10^{12}	-6.20	0.9898
	II	382	Random nucleation	220.6	2.60×10^{18}	101.00	0.9835
	III	526	Random nucleation	89.8	8.10×10^{6}	-120.80	0.9841
$H_2[Tb(DTPA)].H_2O$	I	239	Random nucleation	140.8	3.50×10^{10}	-47.30	0.9789
	II	385	Random nucleation	430.1	3.85×10^{35}	429.70	0.9993
	III	513	Random nucleation	120.6	6.40×10^{8}	-84.40	0.9985
$H_2[Dy(DTPA)].H_2O$	I	241	Random nucleation	190.3	1.90×10^{14}	23.90	0.9936
	II	386	Random nucleation	222.1	6.30×10^{18}	108.40	0.9857
	III	525	Random nucleation	145.5	1.56×10^{10}	-57.90	0.9925
$H_2[Yb(DTPA)].H_2O$	I	246	Random nucleation	207.1	6.95×10^{16}	72.90	0.9991
	II	398	Random nucleation	368.9	1.36×10^{30}	325.20	0.9968
	III	480	Random nucleation	100.5	1.20×10^{8}	-97.90	0.9922

of the europium complex and the lowest value is obtained for the second stage of the lanthanum complex in air. The values of pre-exponential factor are in the range 1.02×10^5 - 2.81×10^{44} s^{-1}, the lowest value being for second stage decomposition of the lanthanum complex in air and the highest value for the second stage decomposition of the europium complex. 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 reactant, while a negative value of entropy of activation indicates that the activated complex is more ordered than the reactant.

All the decomposition stages of the nine complexes of lanthanides with DTPA follow the Mampel equation in air, 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.

Conclusion

All the nine diethylenetriaminepentaacetic acid (DTPA) complexes of lanthanides studied have one water molecule each. These complexes are stable at least upto *ca.* 200 ºC indicating that the water molecules are strongly coordinated to the lanthanide ions. The dehydration and decomposition occur as distinct stages in all the complexes. All the complexes undergo decomposition in three stages in air. The final residue obtained is the stable oxide Ln_2O_3 except for Pr, for which the higher oxide Pr_6O_{11} is formed. The decomposition reactions complete at a temperature range 520-640 ºC.

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