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Thermal Decomposition Studies of Lanthanide(III) Complexes of EDTA

ASHA S. KUMAR* and P. INDRASENAN
Department of Chemistry, University of Kerala, Kariavattom, Trivandrum-695 034, India
E-mail: asha75_skumar@hotmail.com

Thermal decomposition studies of lanthanide(III) complexes of EDTA in nitrogen and air atmospheres are studied using simultaneous TG-DTA. The phenomenological as well as the kinetic aspects of thermal decomposition is described. Based on the observed experimental results, a general mechanism is also proposed. The stability of the complexes in both the atmospheres is also compared.

Key Words: Kinetics, Thermal studies, Lanthanide(III) complexes, EDTA.

INTRODUCTION

Recently, an interest has been developed on the thermal decomposition studies including the kinetics and mechanism of metal complexes[1-5]. 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 this work, the thermal decomposition studies of some EDTA complexes of lanthanides using simultaneous TG-DTA techniques in two distinct atmospheres, *viz.*, air and nitrogen are carried out.

EXPERIMENTAL

All the lanthanide(III) complexones used for the present investigation were prepared by the a general procedure as described[6]. Lanthanide(III) carbonate, (0.5 g; 1.15 mmol) and complexone (H_4EDTA: 0.6 g; 2.3 mmol) were taken in an round bottom flask and 50 mL of water was added. The reaction mixture was shaken vigorously so that the complex was formed with the evolution of carbon dioxide. The solution was filtered to remove any unreacted reagents, if any. The solution was evaporated to dryness on a boiling water bath to get the solid complex, which was dried *in vacuo* over P_2O_5.

The TG, DTG and DTA curves of all the complexes were recorded on a Mettler Toledo TGA/SDTA 851e thermal analysis system in air and nitrogen atmospheres in the temperature region 30-800 ºC. A heating rate of 10 ºC/min and a sample mass of *ca.* 3 mg have been used throughout the

measurement. The plateaus 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[7] 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[8].

RESULTS AND DISCUSSION

Among the nine EDTA complexes of the lanthanides [Ln = La(III), Pr(III), Nd(III), Sm(III), Eu(III), Gd(III), Tb(III), Dy(III) and Yb(III)], all the complexes except that of Yb have only one water molecule each, while the Yb complex has 4 water molecules. 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 simultaneously in almost all the cases except in the case of the Sm complex. More decomposition stages are obtained in air than in nitrogen for a given complex (Tables 1 and 2). Generally, the stability of the complex is greater in nitrogen atmosphere than in air. However, in both the atmospheres, 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. Generally, the decomposition in air takes place in more stages than in nitrogen. All the complexes undergo exothermic reactions in air, while they undergo endothermic reactions in nitrogen (Tables 1 and 2). The exothermicity of the decomposition reactions in air is attributed to oxidative decomposition. The decomposition reactions complete at a lower temperature in air (520-700 ºC) than in nitrogen (660-880 ºC). The stability orders of the complexes in air and in nitrogen are given below (on the basis of the DTG peak temperature of the first decomposition stage as given in parenthesis).

In air: H[Sm(EDTA)]·H_2O < H[Pr(EDTA)]·H_2O < H[La(EDTA)]·H_2O <
(238 ºC) (352 ºC) (354 ºC)
H[Eu(EDTA)]·H_2O < H[Nd(EDTA)]·H_2O < H[Gd(EDTA)]·H_2O <
(362 ºC) (377 ºC) (387 ºC)
H[Tb(EDTA)]·H_2O < H[Dy(EDTA)]·H_2O < H[Yb(EDTA)]·$4H_2O$
(402 ºC) (404 ºC) (408 ºC)

In nitrogen: H[Sm(EDTA)]·H_2O < H[La(EDTA)]·H_2O < H[Pr(EDTA)]·H_2O <
(238 ºC) (374 ºC) (379 ºC)
H[Eu(EDTA)]·H_2O < H[Nd(EDTA)]·H_2O < H[Yb(EDTA)]·$4H_2O$ <
(385 ºC) (389 ºC) (408 ºC)
H[Tb(EDTA)]·H_2O < H[Gd(EDTA)]·H_2O < H[Dy(EDTA)]·H_2O
(409 ºC) (411 ºC) (418 ºC)

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

Complex	Plateaus in TG (ºC)	Decomp. stage	Peak temp. in DTG (ºC)	Peak widths in DTG (ºC)	Peak temp. in DTA (ºC)	Peak width in DTA (ºC)	Mass loss (%)		Residue
							TG	Calcd.	
$H[La(EDTA)]\cdot H_2O$	Upto 220	I	354	300-380	356 (exo)	320-380	32.1	-	-
	After 680	II	495	440-540	496(exo)	480-520	52.5	-	-
		III	674	620-720	672(exo)	650-690	62.3	63.7	La_2O_3
$H[Pr(EDTA)]\cdot H_2O$	Upto 200	I	352	280-400	356(exo)	320-380	42.6	-	-
	After 520	II	491	460-540	488(exo)	460-500	62.8	62.4	Pr_6O_{11}
$H[Nd(EDTA)]\cdot H_2O$	Upto 260	I	377	340-420	378(exo)	340-400	34.3	-	-
	After 650	II	442	420-460	440(exo)	420-480	48.9	-	-
		III	510	480-540	488(exo)	480-500	61.3	63.1	Nd_2O_3
$H[Sm(EDTA)]\cdot H_2O$	Upto 220	I	238	220-280	242(endo)	220-280	4.3	3.8	HSm[EDTA]
	260-290	II	371	340-420	378(exo)	360-400	47.8	-	-
	After 650	III	562	520-580	570(exo)	540-600	62.1	62.3	Sm_2O_3
$H[Eu(EDTA)]\cdot H_2O$	Upto 270	I	362	340-370	363(exo)	340-370	12.7	-	-
	After 650	II	385	370-420	390(exo)	380-410	40.4	-	-
		III	425	420-460	424(exo)	410-430	60.1	62.1	Eu_2O_3
$H[Gd(EDTA)]\cdot H_2O$	Upto 340	I	387	320-420	388(exo)	340-400	40.0	-	-
	After 650	II	457	420-500	456(exo)	440-480	60.0	61.4	Gd_2O_3
$H[Tb(EDTA)]\cdot H_2O$	Upto 340	I	402	360-420	404(exo)	360-420	35.7	-	-
	After 700	II	447	440-520	447(exo)	430-470	60.0	61.1	Tb_2O_3
$H[Dy(EDTA)]\cdot H_2O$	Upto 350	I	404	380-440	406(exo)	380-420	41.5	-	-
	After 650	II	449	420-500	450(exo)	430-480	60.5	60.7	Dy_2O_3
$H[Yb(EDTA)]\cdot 4H_2O$	Upto 370	I	408	380-440	408(exo)	360-420	42.8	-	-
	After 630	II	460	420-500	460(exo)	440-470	63.7	63.4	Yb_2O_3

TABLE-2
THERMAL DECOMPOSITION DATA OF LANTHANIDE(III) COMPLEXES WITH EDTA IN NITROGEN

Complex	Plateaus in TG (ºC)	Decomp. stage	Peak temp. in DTG (ºC)	Peak widths in DTG (ºC)	Peak temp. in DTA (ºC)	Peak width in DTA (ºC)	Mass loss (%)		Residue
							TG	Calcd.	
$H[La(EDTA)].H_2O$	Upto 220 After 700	I	374	340-440	376(endo)	360 - 380	66.80	63.7	La_2O_3
$H[Pr(EDTA)].H_2O$	Upto 200 After 800	I	379	360-420	379(endo)	360 - 400	64.1	62.4	Pr_6O_{11}
$H[Nd(EDTA)].H_2O$	Upto 260 After 660	I	389	340-440	390(endo)	370-400	64.3	63.1	Nd_2O_3
$H[Sm(EDTA)].H_2O$	Upto 230 260-320 After 880	I II	238 397	220-240 340-460	246(endo) 397(endo)	230-260 380-420	4.4 66.6	3.8 62.3	H[Sm(EDTA)] Sm_2O_3
$H[Eu(EDTA)].H_2O$	Upto 280 After 800	I II	385 571	360-420 500-580	386(endo)	360-400	38.2 58.7	- 62.1	- Eu_2O_3
$H[Gd(EDTA)].H_2O$	Upto 360 After 880	I	411	380-460	411(endo)	380-420	62.0	61.4	Gd_2O_3
$H[Tb(EDTA)].H_2O$	Upto 350 After 700	I II	409 514	380-440 460-600	402(endo)	400-430	39.0 62.9	- 61.1	- Tb_2O_3
$H[Dy(EDTA)].H_2O$	Upto 380 After 800	I	418	380-460	425(endo)	400-440	58.3	60.7	Dy_2O_3
$H[Yb(EDTA)].4H_2O$	Upto 370 After 860	I	408	380-440	414(endo)	400-430	63.2	63.4	Yb_2O_3

Kinetics and mechanism of thermal decomposition reactions: The kinetics and mechanism of thermal decomposition reactions of the nine EDTA complexes of lanthanides have been studied using the Coats-Redfern equation[7] and the mechanistic equations proposed by Satava[8]. The kinetic parameters calculated using the Coats-Redfern equation for the decomposition of these complexes in air and in nitrogen are given in Tables 3 and 4. The complexes of La, Nd, Sm and Eu undergo decomposition in three stages and the complexes of Pr, Gd, Dy, Tb and Yb undergo decomposition in two stages in air, while the complexes of Sm, Eu and Tb decompose in two stages and the complexes of La, Pr, Nd,Gd, Dy and Yb decompose in single stage in nitrogen.

The values of order parameter for the decomposition of the nine EDTA complexes of lanthanides in air lie in the range of 0.6 - 2.5, while they lie in the range of 0.6-2.3 in nitrogen atmosphere. The values of activation energy for the decomposition reactions of the complexes are of the order of a few hundreds in most cases and these values are in the range 77.3-588.4 kJ mol^{-1} in air and 88.2-616.9 in nitrogen (Tables 5 and 6). The highest value of activation energy is required for the first decomposition stage of the terbium complex in nitrogen and the lowest value for the second decomposition stage of the europium complex in air. The values of pre-exponential factor are in the range 4.68×10^6 to 6.23×10^{48}, the lowest value being for the second decomposition stage of the europium complex in air and the highest value for the first decomposition stage of the terbium complex in nitrogen. The values of entropy of activation are the reflections of the values of pre-exponential factor (Tables 5 and 6). 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 of entropy of activation indicates that the activated complex is more ordered than the reactants.

Conclusion

All the decomposition stages of the nine complexes of lanthanides [Ln = La(III), Pr(III), Nd(III), Sm(III), Eu(III), Gd(III), Tb(III), Dy(III) and Yb(III)] with EDTA 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.

TABLE-3
KINETIC PARAMETERS OF LANTHANIDE(III) COMPLEXES WITH EDTA IN AIR USING COATS-REDFERN EQUATION

Complex	Decomp. stage	Ts (°C)	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)
$H[La(EDTA)].H_2O$	I	354	1.1	242.2	1.69×10^{21}	155.20	0.9996
	II	495	1.1	172.5	4.01×10^{12}	-11.50	0.9947
	III	674	0.7	241.1	1.42×10^{14}	16.430	0.9824
$H[Pr(EDTA)].H_2O$	I	352	1.4	306.4	5.18×10^{26}	260.40	0.9947
	II	491	1.8	588.4	5.37×10^{41}	546.20	0.9997
$H[Nd(EDTA)].H_2O$	I	377	1.3	296.5	8.08×10^{24}	225.40	0.9994
	II	442	1.7	317.2	6.89×10^{23}	203.70	0.9980
	III	510	1.9	196.2	2.20×10^{14}	2.60	0.9983
$H[Sm(EDTA)].H_2O$	I	238	1.0	136.2	3.90×10^{8}	-84.80	0.9882
	II	371	1.2	362.5	2.55×10^{30}	330.80	0.9994
	III	562	0.8	244.3	7.50×10^{15}	52.60	0.9995
$H[Eu(EDTA)].H_2O$	I	362	2.5	186.1	5.93×10^{16}	69.91	0.9933
	II	385	1.3	77.3	4.68×10^{6}	-123.70	0.9940
	III	425	1.4	124.6	7.32×10^{9}	-63.10	0.9995
$H[Gd(EDTA)].H_2O$	I	387	1.1	413.3	6.14×10^{33}	395.30	0.9998
	II	457	2.0	353.5	2.51×10^{26}	253.10	0.9992
$H[Tb(EDTA)].H_2O$	I	402	0.6	310.4	1.29×10^{25}	229.00	0.9976
	II	447	1.7	447.9	2.52×10^{33}	387.20	0.9997
$H[Dy(EDTA)].H_2O$	I	404	1.5	433.8	7.96×10^{34}	416.40	0.9968
	II	449	1.5	312.0	2.30×10^{33}	386.40	0.9998
$H[Yb(EDTA)].4H_2O$	I	408	1.1	321.0	1.13×10^{26}	247.10	0.9832
	II	460	1.1	444.1	3.66×10^{14}	371.00	0.9871

TABLE-4
KINETIC PARAMETERS OF LANTHANIDE(III) COMPLEXES WITH EDTA IN NITROGEN USING COATS-REDFERN EQUATION

Complex	Decomp. stage	Ts (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)
$H[La(EDTA)].H_2O$	I	374	1.8	208.6	5.26×10^{17}	87.9	0.9965
$H[Pr(EDTA)].H_2O$	I	379	1.1	218.9	1.07×10^{18}	93.7	0.9992
$H[Nd(EDTA)].H_2O$	I	389	1.1	270.0	2.54×10^{22}	177.4	0.9896
$H[Sm(EDTA)].H_2O$	I	238	1.0	91.9	2.32×10^{4}	165.8	0.9979
	II	397	1.2	411.9	1.97×10^{33}	385.8	0.9979
$H[Eu(EDTA)].H_2O$	I	385	0.6	88.2	4.08×10^{7}	-105.7	0.9833
	II	571	1.8	564.3	1.35×10^{36}	438.1	0.9953
$H[Gd(EDTA)].H_2O$	I	411	1.2	118.1	7.98×10^{9}	-62.2	0.9953
$H[Tb(EDTA)].H_2O$	I	409	1.7	616.9	6.23×10^{48}	682.4	0.9989
	II	514	2.0	285.5	3.39×10^{20}	140.7	0.9946
$H[Dy(EDTA)].H_2O$	I	418	2.3	607.8	3.92×10^{47}	659.2	0.9979
$H[Yb(EDTA)].4H_2O$	I	408	0.9	494.9	8.86×10^{38}	493.8	0.9926

TABLE-5
KINETIC PARAMETERS OF LANTHANIDE(III) COMPLEXES WITH EDTA IN NITROGEN USING MECHANISM-BASED EQUATION

Complex	Decomp. stage	Ts (ºC)	Mechanism	Activation energy, E (kJ mol^{-1})	Pre-exponential factor, A (s^{-1})	Entropy of activation, ΔS (JK^{-1} mol^{-1})	Correlation coefficient (r)
$H[La(EDTA)].H_2O$	I	374	Random nucleation	200.5	5.20×10^{17}	87.8	0.9902
$H[Pr(EDTA)].H_2O$	I	379	Random nucleation	210.8	1.01×10^{18}	93.3	0.9980
$H[Nd(EDTA)].H_2O$	I	389	Random nucleation	274.8	5.61×10^{22}	183.9	0.9988
$H[Sm(EDTA)].H_2O$	I	238	Random nucleation	91.9	2.32×10^{4}	-165.8	0.9979
	II	397	Random nucleation	388.6	2.48×10^{25}	234.5	0.9929
$H[Eu(EDTA)].H_2O$	I	385	Random nucleation	88.2	4.08×10^{7}	-105.7	0.9754
	II	571	Random nucleation	422.9	1.50×10^{36}	438.9	0.9871
$H[Gd(EDTA)].H_2O$	I	411	Random nucleation	120.5	6.80×10^{9}	-63.5	0.9546
$H[Tb(EDTA)].H_2O$	I	409	Random nucleation	498.9	5.65×10^{48}	681.5	0.9906
	II	514	Random nucleation	214.2	2.02×10^{20}	135.7	0.9854
$H[Dy(EDTA)].H_2O$	I	418	Random nucleation	599.8	3.86×10^{47}	659.0	0.9911
$H[Yb(EDTA)].4H_2O$	I	408	Random nucleation	508.7	1.09×10^{34}	399.8	0.9926

TABLE-6
KINETIC PARAMETERS OF LANTHANIDE(III) COMPLEXES WITH EDTA IN AIR USING MECHANISM-BASED EQUATION

Complex	Decomp. stage	Ts (ºC)	Mechanism	Activation energy, E (kJ mol^{-1})	Pre-exponential factor, A (s^{-1})	Entropy of activation, ΔS (JK^{-1} mol^{-1})	Correlation coefficient (r)
H[La(EDTA)].H_2O	I	354	Random nucleation	232.4	2.29×10^{21}	157.80	0.9995
	II	495	Random nucleation	167.3	1.60×10^{12}	-19.10	0.9947
	III	674	Random nucleation	269.2	2.13×10^{14}	19.80	0.9804
H[Pr(EDTA)].H_2O	I	352	Random nucleation	263.7	9.32×10^{26}	265.20	0.9934
	II	491	Random nucleation	456.2	2.21×10^{41}	538.70	0.9963
H[Nd(EDTA)].H_2O	I	377	Random nucleation	272.6	2.49×10^{24}	215.60	0.9984
	II	442	Random nucleation	258.2	2.30×10^{23}	195.10	0.9923
	III	510	Random nucleation	137.5	1.80×10^{14}	19.90	0.9939
H[Sm(EDTA)].H_2O	I	238	Random nucleation	136.2	3.90×10^{8}	-84.80	0.9939
	II	371	Random nucleation	336.8	1.74×10^{30}	327.60	0.9988
	III	562	Random nucleation	261.7	1.08×10^{15}	34.30	0.9898
H[Eu(EDTA)].H_2O	I	362	Random nucleation	160.5	2.43×10^{16}	62.50	0.9912
	II	385	Random nucleation	50.5	4.50×10^{5}	-140.50	0.9938
	III	425	Random nucleation	130.8	1.15×10^{4}	-174.20	0.9633
H[Gd(EDTA)].H_2O	I	387	Random nucleation	399.3	4.37×10^{26}	278.40	0.9998
	II	457	Random nucleation	253.5	7.50×10^{26}	262.10	0.9916
H[Tb(EDTA)].H_2O	I	402	Random nucleation	639.1	7.79×10^{25}	243.90	0.9977
	II	447	Random nucleation	339.5	2.51×10^{33}	387.10	0.9727
H[Dy(EDTA)].H_2O	I	404	Random nucleation	400.5	1.50×10^{34}	402.50	0.9988
	II	449	Random nucleation	289.9	2.41×10^{33}	386.80	0.9948
H[Yb(EDTA)].$4H_2O$	I	408	Random nucleation	315.0	2.64×10^{26}	254.00	0.9672
	II	460	Random nucleation	361.7	3.64×10^{14}	26.40	0.9871

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