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THERMAL DECOMPOSITION STUDIES. PART XIII. KINETICS OF THE THERMAL DECOMPOSITION OF THE OXALATES OF THE RARE EARTHS, YTTRIUM AND TITANIUM

K.G. NAIR, V.V. SREERAJAN and V.S.V. NAYAR

Travancore Titanium Products Ltd., Trivandrum-695 021 (India)

C.G.R. NAIR *

Department of Chemistry, University of Kerala, Trivandrum-695 001 (India)

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ABSTRACT

The thermal decomposition behaviour of the oxalates of La, Ce, Pr, Nd, Sm, Gd, Dy, Y and Ti was studied in detail by TG, DTG and DTA. The kinetic parameters (energy and entropy of activation) for the important stages of dehydration and decomposition were evaluated from TG traces by using the Coats—Redfern equation and the modified Coats—Redfern equation.

INTRODUCTION

In the course of a programme to study the thermal decomposition of intimate mixtures of titanium oxalate and oxalates of lanthanides as a feasible route, inter alia, towards the synthesis of mixed oxides of titanium and lanthanides, it became desirable to investigate the decomposition pattern of each individual oxalate. Although some extensive studies had been carried out earlier on the thermal behaviour of oxalates of lanthanides and yttrium, most of these studies were purely phenomenological [1—14]. Only a few kinetic studies have been carried out [9,15,16]. A scrutiny of the results published by earlier workers [5—25] revealed several contradictions and conflicting claims. Only preliminary studies have been carried out [26—33] on the thermal decomposition of titanyl oxalates and some peroxytitanyl oxalates. A systematic study of the kinetics of the thermal decomposition of the oxalates of the rare earths, yttrium and titanium was therefore undertaken. In the present paper, we report the results of our studies on the oxalates of La, Ce, Pr, Nd, Sm, Gd, Dy, Y and Ti in an atmosphere of static air. (Static air was employed in order to simulate the conditions programmed for the synthesis of mixed metal oxides via oxalate decomposition.)

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* To whom correspondence should be addressed.

EXPERIMENTAL

Preparation of rare earth oxalates

The oxalates of La, Ce, Pr, Nd, Sm, Gd, Dy and Y were prepared by standard methods [5,34,35]. The rare earth oxides (about 0.5 g) were dissolved in 5 ml conc. HNO_3. (Dissolution of cerium oxide in nitric acid is facilitated by the addition of 2 ml of 1% hydrofluoric acid which acts as a catalyst [35].) The solutions were diluted to 100 ml and 50 ml of a saturated solution of oxalic acid was added at room temperature (30 ± 2°C). The solutions were stirred vigorously, heated to boiling and then cooled. The precipitated oxalates were filtered off and washed with a 2% aqueous solution of oxalic acid, followed by distilled water, alcohol and finally ether before being dried over anhydrous calcium chloride.

Preparation of titanyl oxalate [36]

Titanium tetrachloride in HCl was hydrolysed by adding slowly to an ice-cooled solution of 5% aqueous ammonia. The orthotitanic acid formed was filtered and washed repeatedly with cold water until it was free from ammonia. The precipitate was dissolved in a saturated solution of aqueous oxalic acid and evaporated at 50—60° to a small volume. Titanyl oxalate was precipitated when absolute alcohol was added to this solution. The oxalate was filtered, washed with alcohol and dried over calcium chloride.

Purity

The purities of the oxalates were determined by the analysis of the metals by ignition of weighed samples to the stable oxides. All the oxalates of the lanthanides were decahydrates. Yttrium oxalate was obtained as a nonahydrate. Titanyl oxalate had the composition $TiO(C_2O_4) \cdot 3.5\ H_2O$. Analysis data are given in Table 1.

TABLE 1

Analysis data

Sample No.	Oxalate	Metal (%)	
		Calcd.	Found
1	La	45.14	44.55
2	Ce	47.53	47.86
3	Pr	46.99	46.31
4	Nd	45.93	45.69
5	Sm	46.81	46.91
6	Gd	47.78	47.52
7	Dy	48.49	48.81
8	Y	37.39	37.59
9	Ti	22.29	22.41

Apparatus [37,38]

A Stanton simultaneous TG—DTA thermobalance, model TRO1, with 0.1 mg sensitivity was used. A heating rate of 4°C min^{-1} and a chart speed of 3 in. h^{-1} were used throughout and sample masses of 30 mg were uniformly employed to give consistent and comparable data. Samples were finely powdered in an agate mortar and placed in deep cylindrical dimpled Pt crucibles (8 mm deep and 6.2 mm diameter). The sample temperature was measured directly by a Pt/Pt—Rh thermocouple, the head of which was placed in the dimple of the crucible. As reference substance for DTA, α-Al_2O_3 was used.

Pyrolysis experiments

Independent pyrolyses were carried out by heating weighed samples of the oxalates in open porcelain crucibles to a temperature of ~800°C. The percentage loss of weight after completion of the pyrolysis was calculated from the weights of the residues.

TREATMENT OF DATA

The instrumental TG curves were redrawn as the mass vs. temperature (TG) curves as well as the rate of loss of mass vs. temperature (DTG) curves. The curves were drawn using standard curve sets. The plateaux and reaction intervals in TG, the peak temperatures in DTG and DTA, and the peak widths in DTA were noted and compared.

Determination of the order of reaction

The order of reaction, n, was found using the equation suggested by Horowitz and Metzger

$$C_s = n^{1/(1-n)} \tag{1}$$

where n is the order of the reaction, C_s is the weight fraction present at the temperature T_s corresponding to the DTG peak. As described earlier [38], a "master curve" was constructed and n obtained from the determined values of C_s.

Evaluation of the kinetic parameters

The kinetic parameters for the dehydration and main decomposition stages were evaluated using the Coats—Redfern equation [39] as well as the modified Coats—Redfern equation [40]. The Coats—Redfern equation was used in the form

$$\log \frac{g(\alpha)}{T^2} = \log \frac{AR}{\phi E} - \frac{E}{2.303RT} \tag{2}$$

TABLE 2

Plateaux, peaks, reaction intervals and peak widths in TG, DTG and DTA curves

Compound	Plateaux in TG (°C)	Peaks in DTG (°C)[a]	Reaction intervals in TG (°C)	Peaks in DTA (°C)[a]		Peak widths in DTA (°C)
Lanthanum oxalate	Up to 120	185 s	120—220	165 endo	s	100—205
	220—380	412 s	380—460	380 exo	s	365—415
		470 w(sh)	460—480	455 exo	w	425—480
	480—660	695 m(br)	660—760	705 exo	m(br)	685—750
	Above 760					
Cerium oxalate	Up to 170	211 s	170—260	187 endo	s	140—220
	250—270	341 s	270—370	320 exo	s	280—380
	Above 370					
Praseodymium oxalate	Up to 140	200 s	140—240	185 endo	s	120—225
	240—380	408 s	380—450	385 exo	s	355—400
		466 w(sh)	450—480	415 exo	m	400—465
	480—500	529 w	500—560	475 exo	w	465—515
	Above 560					
Neodymium oxalate	Up to 150	198 s	150—230	197 endo	s	125—225
	230—250	261 m	250—290	259 endo	m	225—305
	290—390	422 s	390—460	405 exo	s	395—455
		495 m(br)	460—530	535 exo	s(br)	465—605
	530—590	620 m(br)	590—680	650 exo	w(br)	625—705
	Above 680					
Samarium oxalate	Up to 140	200 s	140—220	185 endo	m	140—235
	220—240	269 m	240—300	265 endo	m	235—290
	300—380	428 s	380—540	408 exo	s	385—425
	540—570	591 m	570—640	560 exo	s	490—580
	Above 640					
Gadolinium oxalate	Up to 120	163 m	120—200	168 endo	m	115—195
		226 m	200—245	225 endo	m	205—235
		270 s	245—280	265 endo	s	245—285
	280—380	438 s	380—540	427 exo	s	405—445
	540—560	590 m	560—640	583 exo	s	505—595
	Above 640					
Dysprosium oxalate	Up to 100	138 s	100—160	145 endo	s	110—165
	160—170	197 m	170—210	225 endo	w	185—245
	210—330	363 m	330—380	355 endo	w	325—365
		430 s	380—490	420 exo	s	395—440
	490—500	522 m	500—650	525 exo	s	480—550
	Above 650					
Yttrium oxalate	Up to 90	132 s	90—105	153 endo	m	110—175
		187 m	105—220	195 endo	w	185—230
	220—360	383 m	360—395	392 endo	m	350—400
		427 s	395—480	425 exo	s	400—460
	480—550	601 m	550—650	605 exo	m	530—620
	Above 650					
Titanyl oxalate	Up to 60	105 m	60—170	110 endo	w	60—180
		296 s	170—330	290 endo	s	180—305
				320 exo	m	305—340
	330—500	538 m	500—580	540 exo	m	500—570
	Above 580					

[a] Abbreviations: exo = exothermic; endo = endothermic; w = weak; m = medium; s = strong; vs = very strong; sh = shoulder; br = broad.

TABLE 3

Pyrolysis data

Substance	After Stage I	After Stage II	After Stage III	After Stage IV	Final		Mass loss (%)				
							After Stage I	After Stage II	After Stage III	After Stage IV	Final
La oxalate	$La_2(C_2O_4)_3$	La_2O_3, $2CO_2$	La_2O_3, CO_2		La_2O_3	TG	23.34	43.34	47.34		54.67
						Calc.	24.94	42.67	48.77		54.86
						Pyrolysis					55.45
Ce oxalate	$Ce_2(C_2O_4)_3$				CeO_2	TG	26.67				52.22
						Calc.	24.85				52.47
						Pyrolysis					52.14
Pr oxalate	$Pr_2(C_2O_4)_3$	Partial loss of CO_2	Pr_2O_3, CO_2		Pr_6O_{11}	TG	24.67	46.0	49.67		53.33
						Calc.	24.80		48.5		53.09
						Pyrolysis					53.69
Nd oxalate	$Nd_2(C_2O_4)_3 \cdot 3H_2O$	$Nd_2(C_2O_4)_3$	Nd_2O_3, $2CO_2$	Nd_2O_3, CO_2	Nd_2O_3	TG	17.93	23.33	41.88	47.00	53.83
						Calc.	17.20	24.57	42.05	47.85	54.07
						Pyrolysis					54.31
Sm oxalate	$Sm_2(C_2O_4)_3 \cdot 3.5H_2O$	$Sm_2(C_2O_4)_3$	Sm_2O_3, CO_2		Sm_2O_3	TG	15.28	23.61	48.61		53.47
						Calc.	15.72	24.19	47.28		53.19
						Pyrolysis					53.09
Gd oxalate	$Gd_2(C_2O_4)_3 \cdot 6H_2O$	$Gd_2(C_2O_4)_3 \cdot 4H_2O$	$Gd_2(C_2O_4)_3$	Gd_2O_3, CO_2	Gd_2O_3	TG	9.26	14.35	22.2	48.15	52.78
						Calc.	9.50	14.25	23.75	46.42	52.22
						Pyrolysis					52.48
Dy oxalate	$Dy_2(C_2O_4)_3 \cdot 4H_2O$	$Dy_2(C_2O_4)_3 \cdot 2H_2O$	$Dy_2(C_2O_4)_3$	Dy_2O_3, CO_2	Dy_2O_3	TG	14.53	17.95	23.08	46.15	51.28
						Calc.	14.05	18.74	23.42	45.79	51.51
						Pyrolysis					51.19
Y oxalate	$Y_2(C_2O_4)_3 \cdot 4H_2O$	$Y_2(C_2O_4)_3 \cdot 2H_2O$	$Y_2(C_2O_4)_3$	Y_2O_3, CO_2	Y_2O_3	TG	15.45	19.94	27.92	55.83	62.81
						Calc.	14.91	20.88	26.84	55.33	62.61
						Pyrolysis					62.41
Ti oxalate	$TiO(C_2O_4) \cdot 2H_2O$	Ti_3CO_8			TiO_2	TG	13.8	56.9			61.9
						Calc.	12.56	56.05			62.82
						Pyrolysis					62.59

TABLE 4

Kinetic parameters

Compound	Decomposition stage	DTG peak temperture (°C)	Order of reaction (n)	Energy of activation, E (kJ mole^{-1})		Pre-exponential factor, A (cm$^{3(n-1)}$ mole$^{(1-n)}$ s^{-1})		Entropy of activation, ΔS (J K^{-1} mole^{-1})		Correlation coefficient (γ)	
				C–R [a]	M C–R [a]	C–R [a]	M C–R [a]	C–R [a]	M C–R [a]	C–R [a]	M C–R [a]
La	I	185	1	112.8	109.2	2.59×10^{10}	9.55×10^{9}	−49.2	−57.4	0.9980	0.9984
oxalate	II	412	3	550.9	545.1	1.04×10^{40}	4.26×10^{39}	514.4	506.9	0.9986	0.9985
	III [b]	470									
	IV	695	3	763.7	755.7	8.85×10^{38}	7.06×10^{38}	491.0	482.6	0.9977	0.9953
Ce	I	211	1	155.9	151.9	2.89×10^{14}	1.03×10^{14}	27.9	19.3	0.9952	0.9948
oxalate	II	341	3	733.2	728.1	6.16×10^{61}	1.93×10^{60}	932.2	903.4	0.9832	0.9830
Pr	I	200	1	135.8	131.9	3.44×10^{12}	1.46×10^{12}	−8.7	−15.9	0.9987	0.9986
oxalate	II	408	3	535.4	529.8	1.32×10^{39}	4.79×10^{38}	497.3	488.8	0.9928	0.9926
	III [b]	466									
	IV	529	3	705.2	698.6	1.11×10^{44}	4.09×10^{43}	590.1	581.9	0.9937	0.9936
Nd	I	198	1	145.6	141.7	6.15×10^{13}	2.23×10^{13}	15.3	6.8	0.9981	0.9980
oxalate	II	261	1	130.7	126.1	2.05×10^{10}	7.13×10^{9}	−52.4	−61.2	0.9970	0.9968
	III	422	3	806.3	800.5	7.06×10^{58}	2.56×10^{58}	874.8	866.4	0.9968	0.9967
	IV [b]	495									
	V	620	3	670.7	663.2	1.24×10^{37}	4.59×10^{36}	456.2	447.7	0.9996	0.9996

Sm	I	200	1	95.7	91.8	1.32×10^{8}	4.66×10^{7}	−93.3	−102.0	0.9996	0.9991
oxalate	II	269	1	268.6	264.1	3.97×10^{23}	1.46×10^{23}	201.9	193.6	0.9961	0.9961
	III	428	3	254.3	248.1	2.68×10^{16}	4.05×10^{16}	62.7	65.9	0.9875	0.9868
	IV	591	3	969.5	962.0	4.54×10^{56}	1.50×10^{56}	831.1	821.8	0.9964	0.9961
Gd	I	163	1	91.1	87.6	3.13×10^{8}	1.13×10^{8}	−85.4	−94.0	0.9989	0.9987
oxalate	II	226	1	142.0	137.9	3.16×10^{12}	1.14×10^{12}	−9.9	−18.4	0.9985	0.9982
	III	270	1	303.8	299.3	1.50×10^{27}	5.22×10^{26}	270.4	261.6	0.9941	0.9940
	IV	438	3	257.9	251.7	3.57×10^{16}	1.20×10^{16}	64.7	55.7	0.9942	0.9938
	V	590	3	655.9	649.4	3.04×10^{37}	1.02×10^{38}	463.9	474.0	0.9795	0.9779
Dy	I	138	1	125.1	121.8	4.93×10^{13}	1.80×10^{13}	14.6	6.2	0.9975	0.9973
oxalate	II	197	1	172.2	168.2	8.31×10^{16}	2.85×10^{16}	75.2	66.3	0.9952	0.9945
	III	363	1	298.6	293.2	1.88×10^{22}	6.38×10^{21}	175.2	166.3	0.9996	0.9987
	IV	430	3	508.9	503.0	5.48×10^{35}	1.95×10^{35}	432.2	423.6	0.9986	0.9986
	V	522	3	590.5	583.8	4.20×10^{36}	1.51×10^{37}	448.1	458.8	0.9979	0.9979
Y	I	132	1	107.6	104.3	3.74×10^{11}	1.34×10^{11}	−25.9	−34.4	0.9997	0.9997
oxalate	II	187	1	98.6	94.8	5.81×10^{8}	2.07×10^{8}	−80.8	−89.3	0.9983	0.9979
	III	383	1	433.2	427.8	2.50×10^{32}	8.12×10^{31}	368.8	359.5	0.9945	0.9944
	IV	427	3	566.1	560.2	1.44×10^{40}	5.26×10^{39}	516.9	508.5	0.9974	0.9974
	V	601	3	657.6	650.4	1.56×10^{37}	5.53×10^{36}	458.3	449.6	0.9972	0.9972
Ti	I	105	1	28.0	24.86	1.301×10^{1}	4.319	−225.6	−234.8	0.9960	0.9946
oxalate	II	296	1	70.8	66.6	6.48×10^{3}	2.48×10^{3}	−177.4	−185.4	0.9880	0.9867
	III [b]	538									

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[a] C—R = Coats—Redfern equation; M C—R = modified Coats—Redfern equation.

[b] Calculation of thermal parameters was not done due to poor resolution of the curve.

where

$g(\alpha) = -\ln(1-\alpha)$ when $n = 1$

and

$g(\alpha) = \dfrac{1-(1-\alpha)^{1-n}}{1-n}$ when $n \neq 1$

and A is the pre-exponential factor, ϕ the heating rate, E the energy of activation, R the gas constant and T the absolute temperature.

The modified Coats—Redfern equation [40] was used in the form

$$\log \frac{g(\alpha)}{T^3} = \log\left(\frac{kR}{h\phi E}\right) + \frac{\Delta S}{2.303R} - \frac{E}{2.303RT} \qquad (3)$$

where k is the Boltzmann constant, h the Planck constant and ΔS the entropy of activation.

Plotting the left-hand side of eqns. (2) and (3) against $1/T$ gave straight line graphs with slopes of $-E/2.303\,R$. The activation energy, E, was thus calculated from the slope. A was calculated from the intercept of the Coats—Redfern plot, while ΔS was calculated from the intercept of the modified Coats—Redfern plot. A knowledge of A enables the evaluation of ΔS and vice versa, as has been shown by earlier workers [26], using the equation

$$A = \frac{k}{h} T_s \, e^{\Delta S/R} \qquad (4)$$

RESULTS

The plateaux and reaction intervals in TG, the peak temperatures in DTG and DTA, and the peak widths in DTA are given in Table 2. Pyrolysis data are presented in Table 3 and the kinetic parameters in Table 4.

THERMAL BEHAVIOUR

Oxalates of the rare earths and yttrium

Lanthanum oxalate shows a stability plateau in TG up to 120°C and four DTG peaks at 185, 412, 470 and 695°C; the DTA peaks are at 165, 380, 455 and 705°C. Dehydration takes place in the temperature range 120—220°C in a single step. The endothermic DTA peak at 165°C (Stage I) corresponds to this dehydration. The decomposition starts at 380°C and an intermediate compound which appears to be La_2O_3, 2 CO_2 is formed at 460°C (Stage II). The oxycarbonate La_2O_3, CO_2 is formed (Stage III) at 480°C and is stable up to 660°C. Further decomposition commences at 660°C and the oxide La_2O_3 is obtained above 760°C. The exothermic peak in DTA at 380°C denotes the oxidative decomposition and the two peaks (exo) at 455 and 705°C denote the decomposition of the oxycarbonates.

Cerous oxalate is stable up to 170°C and the dehydration starts at this temperature. Dehydration is completed in a single stage (Stage I) as in the case of lanthanum and the single endothermic DTA peak at 187°C, which corresponds to the DTG peak at 211°C, denotes the dehydration. The anhydrous oxalate is stable between 250 and 270°C after which decomposition starts. The decomposition is completed in the range 270—370°C and the stable CeO_2 is formed above 370°C. The strong exothermic DTA peak at 320°C represents this oxidative decomposition. In this case, the oxalate appears to be directly converted to the Ce(IV) oxide without forming the oxycarbonate. This could mean either the absence of an intervening carbonate stage or a transient existence for this phase which escapes detection under the present conditions. This unique behaviour, shown only by cerous oxalate, distinguishes it from the other rare earth oxalates in the present study.

Praseodymium oxalate is stable up to 140°C and dehydration starts at this temperature, continuing up to 240°C. The DTG peak is at 200°C. The endothermic DTA peak at 185°C represents this dehydration (Stage I). The anhydrous praseodymium oxalate is stable in the range 240—380°C and it undergoes decomposition at 380—450, 450—480 and 500—560°C. The three DTG peaks at 408, 466 and 529°C correspond to the three exothermic DTA peaks at 385, 415 and 475°C and correspond to the decomposition of the anhydrous oxalate in three stages to the oxide. The final product is Pr_6O_{11}. Stages II and III are very close and the intermediate product has only a transient existence. The identification of the product after Stage II was therefore not possible. The product after Stage III corresponds to Pr_2O_3, CO_2.

Neodymium oxalate decahydrate is stable up to 150°C and the dehydration starts at this temperature resulting in a horizontal weight level corresponding to $Nd_2(C_2O_4)_3 \cdot 3\,H_2O$. The trihydrate loses water in the temperature range 250—290°C. The DTG peaks at 198 and 261°C and the corresponding DTA endothermic peaks at 197 and 259°C represent the two dehydration stages (Stages I and II). There is excellent correspondence between DTG and DTA as far as the first two peaks are concerned. At the first stage, the decahydrate is converted to the trihydrate which, at the second stage, forms the anhydrous salt. The anhydrous oxalate is stable in the range 290—390°C and begins to decompose at 390°C. A decomposition peak occurs at 422°C in DTG and at 405°C (exothermic) in DTA. At this stage, the composition corresponds roughly to partial decomposition of the oxalate.

A broad DTA exothermic peak occurs in the region 465—605°C and there is a broad DTG peak also in this region. This could represent the formation of Nd_2O_3, $2\,CO_2$ (Stage III). At 530°C, the composition is Nd_2O_3, CO_2 (Stage IV).

The final decomposition reaction starts at 590°C and the oxide is formed at 680°C. The exothermic DTA peak at 650°C, which corresponds roughly to the DTG peak at 620°C, denotes this decomposition. The final residue after heating up to 700°C was analysed and found to be Nd_2O_3.

Samarium oxalate is stable up to 140°C and dehydration starts at this temperature. The two DTG peaks at 200 and 269° C, which have close correspondence with the two endothermic DTA peaks at 185 and 265° C, correspond to the two dehydration stages (Stages I and II). The first of these stages represents the transition from $Sm_2(C_2O_4)_3 \cdot 10\,H_2O$ to $Sm_2(C_2O_4)_3 \cdot 3.5\,H_2O$ and the second stage refers to the transition to the anhydrous oxalate. The anhydrous oxalate is stable between 300 and 380° C and undergoes decomposition in two stages (Stages III and IV). The DTG peak at 428° C and the exothermic DTA peak at 408° C correspond to the first-stage decomposition. The product at this stage (Stage III) has the composition Sm_2O_3, CO_2. This oxycarbonate then decomposes to the oxide Sm_2O_3 (Stage IV). The DTG peak at 591° C and the exothermic DTA peak at 560° C denote this decomposition.

Gadolinium oxalate is stable up to 120° C and dehydration starts at this temperature. The three DTG peaks at 163, 226 and 270° C, which are closely paralleled by the three endothermic DTA peaks at 168, 225 and 265° C, correspond to the three dehydration stages I, II and III ($10\,H_2O \rightarrow 6\,H_2O \rightarrow 4\,H_2O \rightarrow$ anhydrous salt). The anhydrous oxalate is stable between 280 and 380° C and undergoes decomposition in two stages. The DTG peak at 438° C and the exothermic DTA peak at 427° C correspond to the first stage of decomposition (Stage IV). The product after this stage appears to be Gd_2O_3, CO_2. This then decomposes to the oxide Gd_2O_3 (Stage V). The DTG peak at 590° C and the exothermic DTA peak at 583° C represent the final stage of decomposition.

Dysprosium oxalate appears to be stable up to 100° C when dehydration begins. The three DTG peaks at 138, 197 and 363° C, which correspond with the three endothermic DTA peaks at 145, 225 and 355° C, refer to the Stages I, II and III of dehydration ($10\,H_2O \rightarrow 4\,H_2O \rightarrow 2\,H_2O \rightarrow$ anhydrous salt). The tetrahydrate is stable in the range 210—330°. The anhydrous oxalate undergoes decomposition in two stages (Stages IV and V). The DTG peak at 430° C and exothermic DTA peak at 420° C represent the first of these (Stage IV). The product obtained at this stage has the rough composition Dy_2O_3, CO_2 which further decomposes to the oxide Dy_2O_3 (Stage V). The DTG peak at 522° C and the exothermic DTA peak at 525° C represent this stage of decomposition.

Yttrium oxalate is stable up to 90° C and dehydration begins at this temperature. The three DTG peaks at 132, 187 and 383° C, paralleled by the three endothermic DTA peaks at 153, 195 and 392° C, correspond to Stages I, II and III of dehydration ($9\,H_2O \rightarrow 4\,H_2O \rightarrow 2\,H_2O \rightarrow$ anhydrous salt). The dihydrate is stable in the range 220—360° C. The anhydrous oxalate undergoes decomposition in two stages (Stages IV and V). The DTG peak at 427° C and the exothermic DTA peak at 425° C represent the first of these stages (Stage IV). The product obtained after this stage appears to be Y_2O_3, CO_2. This further decomposes to the oxide Y_2O_3 (Stage V). The DTG peak at 601° C and the exothermic DTA peak at 605° C represent this stage of decomposition.

Titanyl oxalate, $TiO(C_2O_4) \cdot 3.5\,H_2O$, is stable up to 60° C and the dehydration starts at about this temperature. The DTG peak is at 105° C. The endothermic DTA peak at 110° C represents this dehydration (Stage I) leading to the formation of the dihydrate, $TiO(C_2O_4) \cdot 2\ H_2O$. The dihydrate begins further dehydration accompanied by decomposition. The DTG peak at 296°C represents this stage (Stage II). In DTA, this stage is represented by two close-lying peaks, an endothermic peak at 290°C and an exothermic peak at 320°C. The phase formed at 330°C is a basic carbonate of titanium with the empirical formula Ti_3CO_8 or $TiO(CO_3)$, $2\ TiO_2$ and is stable up to 500°C. Above this temperature, it decomposes to give TiO_2. The DTG peak at 538°C, paralleled by the exothermic peak at 540°C, corresponds to this final stage of decomposition (Stage III).

Mass loss data

Mass loss data are given in Table 3. The final residue is the oxide M_2O_3 for M = La, Nd, Sm, Gd, Dy and Y; it is MO_2 for Ce and Ti and Pr_6O_{11} for Pr. The mass loss data from TG, as well as from independent pyrolysis studies. agree closely with calculated values in all cases. It may be seen from Table 3 that the agreement is satisfactory between the calculated and observed (from TG) values for mass loss data for intermediate stages as well, wherever intermediate stages are sufficiently well-defined.

Kinetic parameters

The kinetic parameters evaluated from the TG traces are given in Table 4. The values of E, ΔS and A using the Coats—Redfern equation and a similar set using the modified Coats—Redfern equation are presented. The correlation coefficients in each case are also shown.

DISCUSSION

Thermal behaviour

A survey of the results in Tables 2 and 3 reveals an interesting fact. The hydrated oxalates of the lighter lanthanides (La, Ce and Pr) undergo single-stage dehydration from the decahydrate to the anhydrous salt. In Nd and Sm, we have two-stage dehydration, whereas in the heavier lanthanides Gd and Dy, we have three-stage dehydration. As expected, Y falls in line with the heavier lanthanides [41] and shows a three-stage dehydration. It is interesting to note that these definitive trends observed in the thermal behaviour are compatible with the well-known increase in coordination ability (e.g. hydration energies) of the lanthanide M^{3+} ion from La to Lu.

The final residues are normal oxides, M_2O_3, in the case of La, Nd, Sm, Gd, Dy and Y. In the case of Pr, it is Pr_6O_{11} and for Ce it is CeO_2. This is not surprising because, under open static air conditions, one expects the most stable oxide to be formed, which is Pr_6O_{11} for Pr and CeO_2 for Ce. The residue for titanyl oxalate is TiO_2 as expected.

A similar, although less clear-cut, tendency could be noted as regards the final decomposition to the oxide stage. The oxide stage is attained at 760°C for La, 680°C for Nd and at about 640°C for Sm, Gd, Dy and Y. This indicates that the thermal stability of the carbonates decreases marginally from La through Nd to Sm, Gd, Dy and Y. Such an order would reflect the increasing Lewis acidities of the M^{3+} ions from La^{3+} to Lu^{3+}. The exceptional behaviour in the case of Ce and Pr could be attributed to the formation of oxides of formulae other than M_2O_3.

The DTA peaks for dehydration are endothermic as expected. In the case of further decompositions, whereas one may expect endothermicity as a general tendency, one finds exothermicity in all the cases. This may be explained by oxidation processes (such as combustion of the liberated CO to CO_2) accompanying the decomposition of the oxalates in the oxidizing atmosphere (static air) employed for the studies. (It is well known that CaC_2O_4 gives exothermic DTA peaks in air, whereas in nitrogen, the DTA peaks reveal their true endothermicity.) In the present studies, static air was deliberately employed as mentioned earlier.

Kinetic parameters

Lanthanides and yttrium

The first dehydration stages are found to have E values of the order of ~100 kJ $mole^{-1}$. The second dehydration stages also generally have values of 100—200 kJ $mole^{-1}$, although the third dehydration stages (e.g. Gd and Y) have higher values (300—450 kJ $mole^{-1}$). This implies that the dehydration of the lower hydrate is kinetically less favoured than that of the higher hydrates.

The decomposition stage, especially the final ones leading to oxide formation, show higher values of E (700—800 kJ $mole^{-1}$). This is to be expected because these decomposition stages involve rupture of stronger bonds than in the case of dehydration. It is difficult to draw definitive conclusions from ΔS and A data which must await further theoretical developments in this field. One may note, however, that the dehydrations generally tend to have lower values of ΔS and A. A negative value for ΔS further shows a more ordered activated complex and a less than normally fast reaction. On the other hand, positive values of ΔS indicate less ordered activated complexes and faster than normal reactions [42].

Titanyl oxalate

The first dehydration stage of titanyl oxalate has a low value for the energy of activation (~30 kJ $mole^{-1}$), whereas the second stage has a slightly higher value (~70 kJ $mole^{-1}$). It may be noted that the order of magnitude of both values is the same as, or one less than, that for similar dehydration stages of lanthanide oxalates.

The values for the entropy of activation for the dehydration stages of hydrated titanyl oxalate are found to be negative, indicating that the activated complex is more ordered than the reactants and that the reaction is less than normally fast [42].

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