THERMAL DECOMPOSITION OF RARE-EARTH TRIOXALATOCOBALTATES

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ABSTRACT

The thermal decomposition of rare-earth trioxalatocobaltates $LnCo(C_2O_4)_3 \cdot x\, H_2O$, where Ln = La, Pr, Nd, has been studied in flowing atmospheres of air/oxygen, argon/nitrogen, carbon dioxide and a vacuum. The compounds decompose through three major steps, viz. dehydration, decomposition of the oxalate to an intermediate carbonate, which further decomposes to yield rare-earth cobaltite as the final product. The formation of the final product is influenced by the surrounding gas atmosphere. Studies on the thermal decomposition of photodecomposed lanthanum trioxalatocobaltate and a mechanical mixture of lanthanum oxalate and cobalt oxalate in 1 : 2 molar ratio reveal that the decomposition behaviour of the two samples is different. The drawbacks of the decomposition scheme proposed earlier have been pointed out, and logical schemes based on results obtained by TG, DTA, DTG, supplemented by various physico-chemical techniques such as gas and chemical analyses, IR and mass spectroscopy, surface area and magnetic susceptibility measurements and X-ray powder diffraction methods, have been proposed for the decomposition in air of rare-earth trioxalatocobaltates as well as for the photoreduced lanthanum salt and a mechanical mixture of lanthanum and cobalt oxalates.

INTRODUCTION

Rare-earth perovskites, $LnMO_3$, where Ln = rare-earth or yttrium and M = first-row transition metal like Fe, Co, Mn, Ni and oxides wherein rare-earths are partially substituted by bivalent metals show interesting crystallographic and magnetic properties. Recently, rare-earth cobaltites and manganites have been reported [1] to be good catalysts for the oxidation of carbon monoxide and hydrocarbons and the reduction of oxides of nitrogen. The need for pure, stoichiometric cobaltites led to the development of chemical methods for their preparation. Gallagher [2] has studied the thermal decomposition of rare-earth hexacyanocobaltates and shown that they yield rare-earth cobaltites as the end products. Rare-earth trioxalatocobaltates are promising precursors for the low-temperature production of rare-earth cobaltites. Except for a recent report by Nag and Roy [3], there has been no systematic study on the thermal stability of rare-earth trioxalatocobaltates.

EXPERIMENTAL

Materials

All the reagents were either BDH 'Analar' or E. Merck 'pro analysi' grade. Rare-earth trioxalatocobaltate(III) hydrates are prepared by mixing, with stirring, the rare-earth nitrate solution (2 M) and ammonium trioxalatocobaltate solution (2 M). The mixture is cooled in ice, filtered, the precipitate washed with small portions of ice-cold water, then with acetone and air-dried. The compounds $LnCo(C_2O_4)_3 \cdot x\ H_2O$, where Ln = La, Pr, Nd, have been prepared.

Nag and Roy [3] have employed rare-earth nitrate and potassium trioxalatocobaltate solutions as the reactants. The present study reveals that while the lanthanum salt is practically free from potassium contamination, the praseodymium and neodymium salts obtained by this procedure are heavily contaminated with potassium. Repeated washing with water lowers the potassium content but also reduces the yield. This difficulty is obviated by replacing potassium trioxalatocobaltate with ammonium salt.

METHODS

The procedures for physical studies such as TG, DTA, IR spectroscopy, X-ray powder diffraction and surface area measurements are described in an earlier communication [4].

The rare-earth elements are estimated gravimetrically as oxides. Cobalt is estimated volumetrically by tritation with EDTA at pH 5.6, employing methyl thymol blue as indicator. Oxalate is determined by titration against standard potassium permanganate. Carbonate in the intermediate residues is determined gravimetrically by decomposing it with dilute hydrochloric acid and absorbing the evolved carbon dioxide, after drying, in ascarite. Water content in the compounds is estimated gravimetrically, by decomposing a known weight and absorbing the expelled water in anhydrous magnesium perchlorate. The procedure for evolved gas analysis has been reported earlier [4].

RESULTS

Rare-earth trioxalatocobaltate(III) hydrates have the general formula $Ln[Co(C_2O_4)_3] \cdot x\ H_2O$, where Ln = La, Pr and Nd. The analytical data on these complexes are given in Table 1. All the compounds are green in colour and show absorption at 445 and 625 nm corresponding to six coordinated Co(III). The IR spectra of these compounds are remarkably similar to one another and all the bands can be assigned based on assignments made for the reported oxalato complexes [5]. The principal oxalate bands are: $\nu_{as}(C=O)$ at ~ 1650 cm^{-1}, $\nu_s(C-O) + \nu(C-C)$ at $\sim 1420-1450$ cm^{-1}, $\nu_s(C-O) + \delta(O-C=O)$ at $1290-1350$ cm^{-1}, and $\delta(O-C=O) + \nu(M-O)$ at $800-830$

TABLE 1

Analytical data of the compounds $Ln[Co(C_2O_4)_3] \cdot x\ H_2O$

Compound	Ln (%)		Co (%)	C_2O_4 (%)	H_2O (%)
$La[Co(C_2O_4)_3] \cdot 9\ H_2O$	obs.	22.43	9.45	42.45	26.45
	calc.	22.27	9.44	42.32	25.96
$Pr[Co(C_2O_4)_3] \cdot 8\ H_2O$	obs.	23.15	9.61	43.86	24.25
	calc.	23.05	9.70	43.50	23.73
$Nd[Co(C_2O_4)_3] \cdot 8\ H_2O$	obs.	23.75	9.54	43.68	24.12
	calc.	23.60	9.64	43.20	23.57

cm^{-1}. Lanthanum and praseodymium trioxalatocobaltates are crystalline and their X-ray powder diffraction data are presented in Table 2. Analysis of the data shows that the compounds are of low symmetry class. Neodymium trioxalatocobaltate is poorly crystalline.

TABLE 2

X-Ray powder diffraction data of LCO and PCO

LCO		PCO		
d (Å)	I/I_0	d (Å)	I/I_0	
10.27	60	9.92	20	
9.92	10	7.75	55	
8.68	35	7.49	100	
7.82	10	6.41	15	
7.49	20	5.98	70	
7.01	20	5.82	65	
6.91	10	5.50	20	
5.90	20	5.30	20	
5.40	100	5.24	10	
4.68	25	5.15	20	
4.57	30	4.97	15	
4.03	15	4.84	20	
3.814	15	4.48	60	
3.335	10	4.38	25	
3.195	10	4.28	20	
3.035	9	4.018	60	
2.976	7	3.930	10	
2.937	7	3.750	15	
2.919	10	3.558	10	
2.408	10	3.476	20	
2.336	10	3.263	20	
2.029	10	3.183	15	
1.987	9	3.097	20	
		3.035	15	
		2.891	20	
		2.672	20	
		2.568	20	
		2.396	20	

LANTHANUM TRIOXALATOCOBALTATE(III) NONAHYDRATE(LCO)

Thermograms of lanthanum trioxalatocobaltate(III) nonahydrate(LCO) in flowing atmospheres of oxygen, carbon dioxide, argon and a vacuum are presented in Figs. 1 and 2. Table 3 gives the weight losses and the corresponding temperature ranges for the different steps of decomposition in the various atmospheres. Qualitatively there is a 1 : 1 correspondence between the DTA and DTG plots, implying that every thermal effect is accompanied by a weight loss. The decomposition proceeds through three major steps: dehydration of the hydrate, decomposition of the oxalate to form a carbonate, and decomposition of the carbonate to form the final product, lanthanum cobaltite. The nature of the final product is significantly affected by the surrounding gas atmosphere during the decomposition.

Dehydration of the hydrate

LCO prepared under normal drying conditions contains 9 H_2O mole^{-1} and does not take up excess water with varying atmospheric humidity. The dehydration of the nonahydrate takes place in the temperature range 60—250°C with a peak maximum around 105°C. The different thermograms show weight losses in the range 28.0—33.5%. The theoretical value for dehydration alone is only 25.96% which is far less than that observed. Gas analysis indicates that there is evolution of approximately 1 mole of carbon dioxide per mole of the starting oxalate complex during dehydration. There
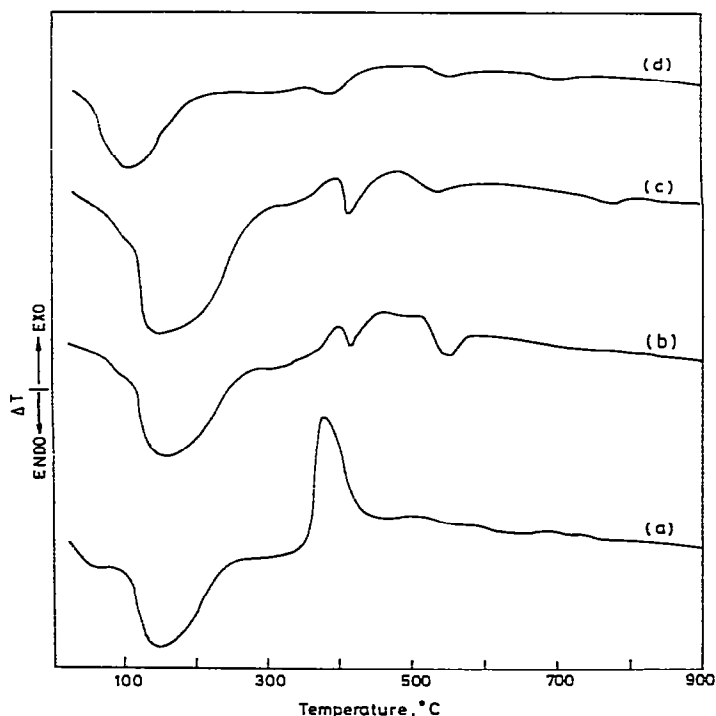

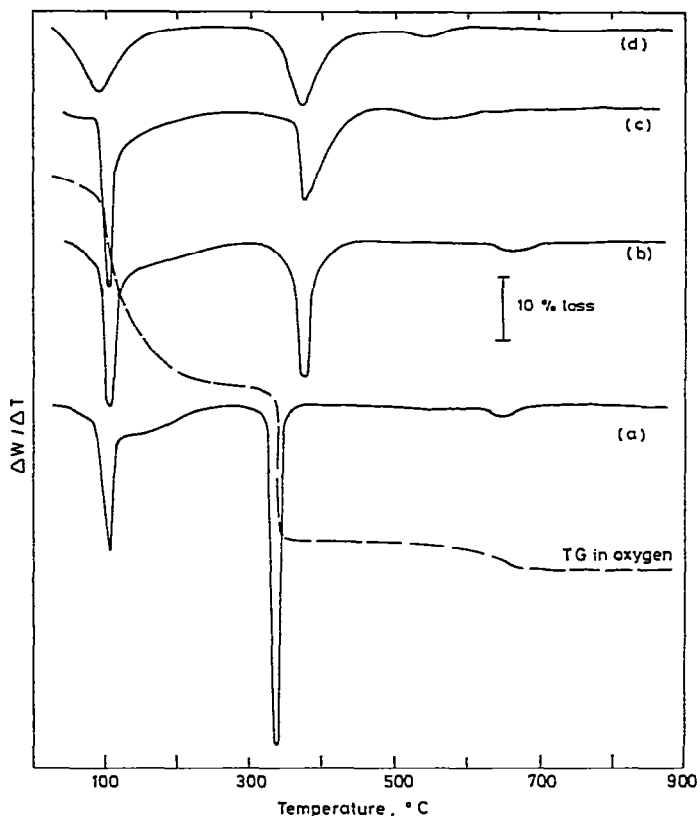Fig. 1. DTA of LCO in (a) oxygen, (b) carbon dioxide, (c) argon, and (d) a vacuum.

Fig. 2. DTG of LCO in (a) oxygen, (b) carbon dioxide, (c) argon, and (d) a vacuum.

is also a change in the colour of the compound from green to pink. The dehydration step is accompanied by an auto-redox process where Co(III) is reduced to Co(II) by the oxidation of 0.5 mole of oxalate per mole of the compound. Such a reduction of Co(III) to Co(II) has been noticed by Wendlandt and Simmons [6] in the thermal decomposition of potassium trioxalatocobaltate. If this is the case, a weight loss of 33.02% is expected corresponding to the loss of 9 H_2O and 0.5 moles of oxalate per mole of the compound, which is comparable to the observed values. LCO heated at 120°C for 3 days becomes completely dehydrated. Dehydration can be achieved partially at room temperature by evacuation. In fact, slow evacuation at 25°C for 12 h results in a weight loss of nearly 15%, but dehydration is invariably accompanied by partial decomposition of oxalate even at room temperature. Dehydration can be achieved at lower temperatures in a vacuum. In a vacuum, dehydration can be achieved at 110°C in about 5—6 h. Dehydration is only partially reversible in that rehydration does not result in the conversion of Co(II) back to Co(III). However, the dehydrated sample, on exposure to water vapour, takes up water to form a heptahydrate. The residue at the end of dehydration has the composition $LaCo(C_2O_4)_{2.5}$. The dehydrated LCO is amorphous to X-rays and has a surface area around 3 m^2 g^{-1}, indicating the non-porous nature of the material. The partially rehydrated material is also amorphous to X-rays.

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TABLE 3

Temperature ranges and weight losses for the decomposition of LCO in different atmospheres

Decomposition step	Calc. % wt. loss	Oxygen		Argon		Carbon dioxide		Vacuum	
		Temp. range (°C)	% Wt. loss	Temp. range (°C)	% Wt. loss	Temp. range (°C)	% Wt. loss	Temp. range (°C)	% Wt. loss
Dehydration of LCO accompanied by initial oxalate decomposition	33.02	60—250	32.5	70—250	33.5	60—250	32.0	50—250	28.0
Main oxalate decomposition	22.28	250—500	22.5	250—475	22.5	250—450	22.5	250—500	28.5
Final decomposition of the carbonate	5.29	500—700	5.5	475—700	5.0	450—700	6.5	500—750	6.0
Total weight loss	60.59		60.5		61.0		61.0		62.5

IR spectra of LCO and dehydrated LCO are presented in Fig. 3. The important band in the spectrum of LCO is the asymmetric stretching mode of the (C—O) group of the oxalate at 1650 cm^{-1}. The IR spectrum of LCO dehydrated at 110°C shows slight differences from that of LCO; there are fewer bands.

Decomposition of the oxalate

The thermal decomposition of the oxalate is a single-step process to yield the carbonate. In the range 250—500°C, a single peak occurs with a weight loss of 22.5%. Analysis of the gases evolved when anhydrous LCO is decomposed at 300°C indicates that both carbon monoxide and carbon dioxide are evolved. This step of oxalate decomposition involves the decomposition of the oxalate, oxidation and/or disproportionation of carbon monoxide, and oxidation of the elemental carbon formed by the disproportionation of carbon monoxide. Therefore, the total weight loss is slightly variable depending on the surrounding atmosphere. The oxalate decomposition is endothermic. In air or oxygen, however, it is an exotherm because of the highly exothermic oxidation of carbon monoxide. The residue at this stage of decomposition has a composition $LaCoO_{3-x}(CO_3)_x$. This residue is black both in oxidizing and non-oxidizing atmospheres or in a vacuum. When the residue is dissolved in dilute hydrochloric acid, black particles of carbon remain undissolved. This carbon results from the partial disproportionation of carbon monoxide. Isothermal heating of LCO at 380°C results in a carbonate of composition $LaCoO_{3-x}(CO_3)_x$. The composition of the residue is obtained by chemical analysis and indicates $x \sim 0.6$, and a weight loss of 56.9% is recorded which is in good agreement with the calculated value of 56.67% for
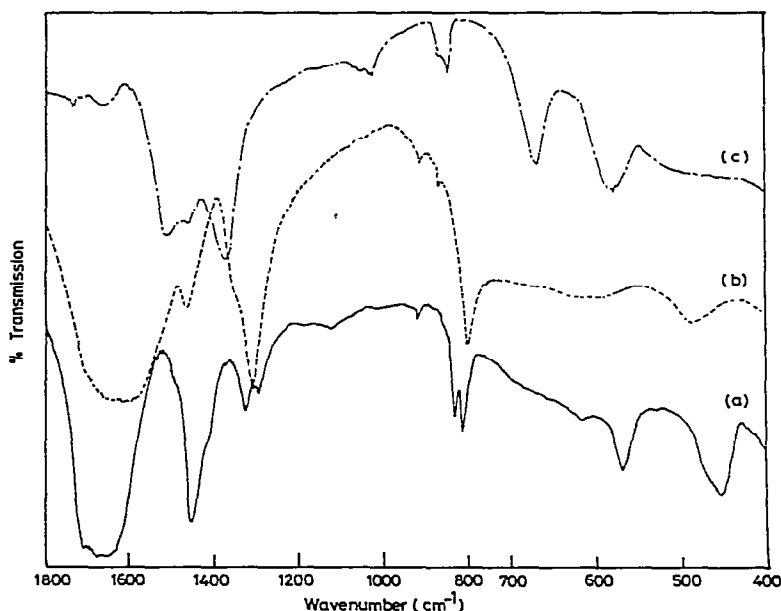

Fig. 3. IR spectra of (a) LCO, (b) $LaCo(C_2O_4)_{2.5}$ and (c) $LaCoO_{3-x}(CO_3)_x$.

the composition with $x = 0.6$. The chemical analysis of the residue gives the following results: La = 52.11, Co = 21.49 and CO_2 = 9.91%; calculated values for $LaCoO_{3-x}(CO_3)_x$, $x = 0.6$ are: La = 51.41, Co = 21.63 and CO_2 = 9.77%. This intermediate oxycarbonate also does not give any X-ray powder diffraction pattern. The weight losses in dynamic experiments more nearly correspond to a value of $x = 0.75$.

The IR spectrum of $LaCoO_{3-x}(CO_3)_x$ (Fig. 3c) does not show any bands due to the oxalate group but shows bands due to the carbonate group. The principal band due to carbonate is in the region 1370—1550 cm^{-1}. In the spectrum there is no band at 2350 cm^{-1} which shows that there is no trapped free carbon dioxide in the carbonate, as is observed in the decomposition of barium titanyl oxalate [4]. Further, the IR spectrum of this intermediate shows the bands due to the carbonate: ν_{as} at 1370—1550 cm^{-1}, ν_s at 1030 cm^{-1} (very weak), the out-of-plane bending mode at 670 cm^{-1} and bond deformation at ~850 cm^{-1}. The IR spectrum is comparable to those of rare-earth oxycarbonates [7]. None of the IR spectra of the residues show absorption in the region 1800—2200 cm^{-1}, indicating that there are no coordinated carbonyl groups or free carbon monoxide.

Decomposition of the intermediate carbonate

The intermediate $LaCoO_{3-x}(CO_3)_x$ decomposes in the temperature range 500—700°C with the release of carbon dioxide giving rise to lanthanum cobaltite in air or oxygen. This is observed as a small endotherm on the thermograms. The decomposition is shifted to a higher temperature in carbon dioxide or a vacuum. This is expected for the decomposition of a carbonate in carbon dioxide but not in a vacuum. The weight loss for this final carbonate decomposition varies from 5.0 to 6.5% compared to the calculated value of 5.29%.

The thermal decomposition of the carbonate is accompanied by a simultaneous growth in the particle size of the product lanthanum cobaltite in air or oxygen, as indicated by the sharp lines in the X-ray powder diffraction pattern of $LaCoO_3$ resulting from the reaction. The products have slightly different d spacings in inert atmospheres like argon or carbon dioxide and a vacuum. The formation of the final product is thus highly influenced by the surrounding atmosphere. Whereas in air, lanthanum cobaltite is the final product of decomposition, in carbon dioxide and in a vacuum, variations are observed in the d spacings, as indicated by the X-ray powder diffraction data which may be attributed to the variations in the oxygen stoichiometries. Moreover, in a vacuum La_2O_3 and CoO are also found to be present in the final product of decomposition along with the cobaltite. $LaCoO_3$ prepared by decomposing LCO in air at 700°C has a surface area of 2.7 $m^2\ g^{-1}$.

Decomposition of photoreduced lanthanum trioxalatocobaltate (PR-LCO)

Like all other trioxalatocobaltates, rare-earth trioxalatocobaltates are photosensitive. On exposure to light or on keeping for a long period, LCO undergoes photoreduction. Green LCO on keeping for a month changes to a pink
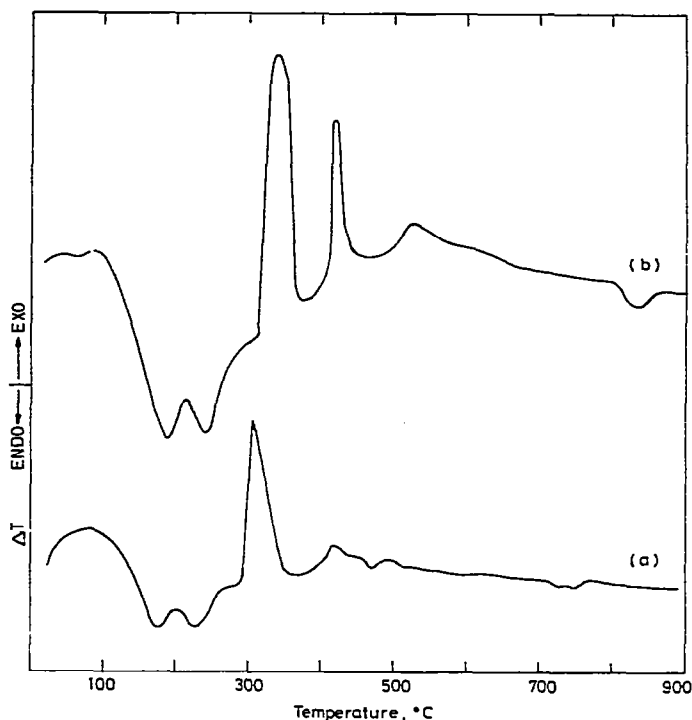
Fig. 4. DTA in air of (a) LCO (photodecomposed), and (b) mixture of LO and CO.

compound which on analysis gives the composition $LaCo(C_2O_4)_{2.5} \cdot 7\ H_2O$ (PR—LCO). This photoreduced solid is paramagnetic and contains divalent cobalt. The composition of this pink residue apparently corresponds to that of a mixture of lanthanum oxalate and cobalt oxalate in the molar ratio 1 : 2. Thermal analysis of the photoreduced LCO has been compared with that of a mechanical mixture of lanthanum oxalate decahydrate(LO) and cobalt oxalate dihydrate(CO) in 1 : 2 molar ratio, with a view to determining the similarity or difference in the mode of decomposition of the two.

Figures 4 and 5 give the DTA and DTG curves for PR-LCO and a mechanical mixture of LO and CO in 1 : 2 molar ratio. Qualitatively, a 1 : 1 correspondence is observed between the DTA and DTG curves for PR-LCO and those for a mechanical mixture of LO and CO, indicating that every thermal effect is accompanied by weight loss in both cases. Table 4 compares the temperature ranges and weight losses in air for PR-LCO and the mechanical mixture of LO and CO. The results indicate that the decomposition modes in the two cases differ significantly.

PR-LCO decomposes in three major steps, viz. dehydration, decomposition of the oxalate to form a carbonate and finally, the decomposition of the carbonate to give lanthanum cobaltite. Dehydration takes place in the temperature range 50—240°C with a weight loss of 23.5% in air as compared to the calculated value of 23.17% for the removal of 7 H_2O mole^{-1}. The DTA and DTG curves show two distinct endotherms in this temperature range, indicating that dehydration takes place in two steps. Decomposition of the
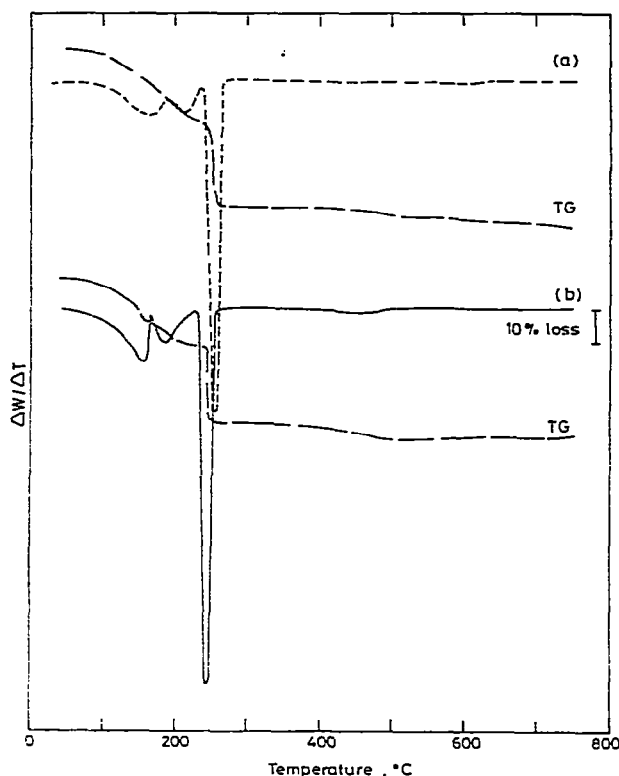
Fig. 5. DTG in air of (a) LCO (photodecomposed), and (b) mixture of LO and CO.

oxalate takes place in the range 240—400°C with a weight loss of 25.5% to give an intermediate oxycarbonate $LaCoO_{3-x}(CO_3)_x$. The observed weight loss agrees very well with the calculated value of 25.56% for $x = 0.75$. The IR spectrum of this compound obtained by isothermal heating at 330°C is

TABLE 4

Thermal decomposition data in air for photoreduced LCO and for a mechanical mixture of lanthanum oxalate and cobalt oxalate in 1 : 2 molar ratio
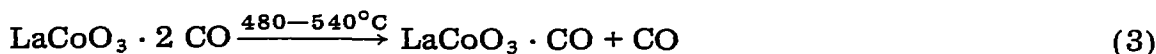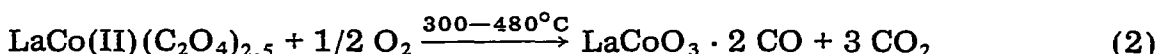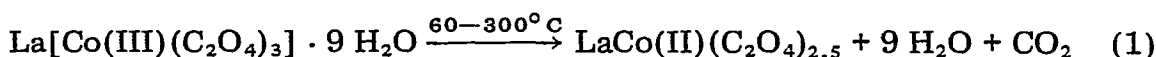
Decomposition step	Calc. % wt. loss	Photoreduced LCO		Mixture of LO and CO	
		Temp. range (°C)	% Wt. loss	Temp. range (°C)	% Wt. loss
Dehydration	23.17	50—240	23.5	50—250	24.5
Decomposition of oxalate to an intermediate carbonate	25.56	240—400	25.5	250—500	25.5
Decomposition of carbonate to oxide	6.07	400—700	6.0	500—700	1.0
Total weight loss	54.80		55.0		51.0

similar to that of the carbonate intermediate formed during the decomposition of LCO. This intermediate carbonate decomposes in the temperature range 400—750°C to give crystalline $LaCoO_3$ as confirmed by the X-ray data of the residue. The observed value of 6.00% is in excellent agreement with the calculated value of 6.07%. The oxalate decomposition takes place in a single step and is exothermic due to the secondary reaction of the carbon monoxide evolved.

The decomposition of a mechanical mixture of LO and CO proceeds in a different way. Dehydration takes place in two steps, as evident from the DTA and DTG curves, in the temperature range 50—250°C with a weight loss of 24.5%. The oxalate decomposition occurs in the temperature range 250—500°C accompanied by a weight loss of 25.5%. However, it is observed that while the DTG shows the oxalate decomposition as a single-step reaction, two clear exotherms are observed in the DTA, indicating that the two oxalates decompose separately. The IR spectrum of the mixture decomposed at 330°C is similar to that of the photoreduced LCO decomposed at the same temperature. However, the X-ray powder diffraction data for the two intermediates are dissimilar, indicating the diverse nature of the compound. A further weight loss of only 1% is observed in the temperature range 500—900°C. The X-ray powder diffraction data of the residue at 900°C reveal lines due to La_2O_3 and Co_3O_4.
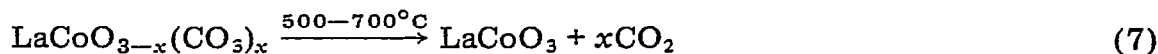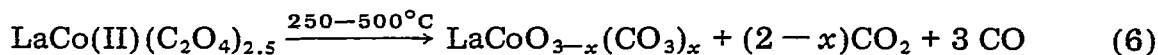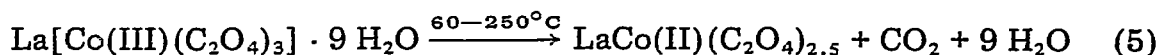
DISCUSSION

So far, the thermal decomposition of rare-earth trioxalatocobaltates(III) has been studied only in air by Nag and Roy [3]. Though a formal scheme has not been spelled out by them, from the weight losses, temperature ranges and the suggested intermediates, the following scheme might represent their results

$$La[Co(III)(C_2O_4)_3] \cdot 9\ H_2O \xrightarrow{60—300°C} LaCo(II)(C_2O_4)_{2.5} + 9\ H_2O + CO_2 \quad (1)$$

$$LaCo(II)(C_2O_4)_{2.5} + 1/2\ O_2 \xrightarrow{300—480°C} LaCoO_3 \cdot 2\ CO + 3\ CO_2 \quad (2)$$

$$LaCoO_3 \cdot 2\ CO \xrightarrow{480—540°C} LaCoO_3 \cdot CO + CO \quad (3)$$

$$LaCoO_3 \cdot CO \xrightarrow{560—640°C} LaCoO_3 + CO \quad (4)$$

Results of the present study substantiate only the first step of dehydration accompanied by partial decomposition of the oxalate. Intermediates of the composition $LaCoO_3 \cdot 2\ CO$ and $LaCoO_3 \cdot CO$ are not substantiated by the IR spectra or the weight loss steps in the present experiments. The IR spectra of the intermediates do not indicate the presence of any carbonyl groups. There is a clear indication of the formation of an oxycarbonate intermediate.

Based on the results of the present investigation, the following scheme is proposed for the decomposition of LCO in air/oxygen.

$$La[Co(III)(C_2O_4)_3] \cdot 9 H_2O \xrightarrow{60-250^\circ C} LaCo(II)(C_2O_4)_{2.5} + CO_2 + 9 H_2O \quad (5)$$

$$LaCo(II)(C_2O_4)_{2.5} \xrightarrow{250-500^\circ C} LaCoO_{3-x}(CO_3)_x + (2-x)CO_2 + 3 CO \quad (6)$$

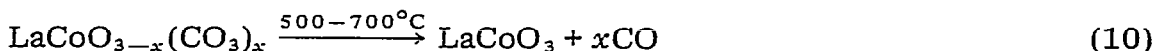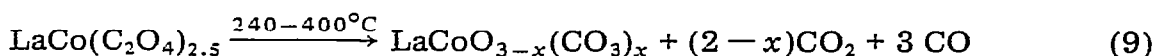$$LaCoO_{3-x}(CO_3)_x \xrightarrow{500-700^\circ C} LaCoO_3 + xCO_2 \quad (7)$$

Equation (5) represents the removal of all the crystal water along with partial oxalate decomposition and a simultaneous reduction of CO(III) to Co(II). The conversion of Co(III) to Co(II) is confirmed by magnetic susceptibility measurements. Green LCO is diamagnetic whereas anhydrous LCO of composition $LaCo(C_2O_4)_{2.5}$ is paramagnetic.

Equation (6) represents the main oxalate decomposition. The gaseous products of this decomposition are carbon monoxide and carbon dioxide, which should be present in the limiting ratio 1 : 3 (if $x = 1$). However, secondary reaction of carbon monoxide influences the ratio of the two gases as well as the thermal effects. Because of this disproportionation of carbon monoxide, the ratio of $CO : CO_2$ is expected to be lower than 3 and the actual ratio observed is less than 1. Disproportionation of carbon monoxide can be quite extensive in the presence of transition metal ions. Glassner and Steinberg [8] report that in the thermal decomposition of lanthanide oxalates as much as 70% of carbon monoxide disproportionates. Hence, any deviation observed in the $CO : CO_2$ ratio may be attributed to the extensive disproportionation of carbon monoxide.

The final decomposition is a true thermal decomposition of the carbonate $LaCoO_{3-x}(CO_3)_x$ resulting in the formation of crystalline lanthanum cobaltite, $LaCoO_3$.

The data on PR-LCO can be explained by the following decomposition scheme

$$LaCo(II)(C_2O_4)_{2.5} \cdot 7 H_2O \xrightarrow{50-240^\circ C} LaCo(C_2O_4)_{2.5} + 7 H_2O \quad (8)$$

$$LaCo(C_2O_4)_{2.5} \xrightarrow{240-400^\circ C} LaCoO_{3-x}(CO_3)_x + (2-x)CO_2 + 3 CO \quad (9)$$

$$LaCoO_{3-x}(CO_3)_x \xrightarrow{500-700^\circ C} LaCoO_3 + xCO \quad (10)$$

where $x = 0.75$.

The decomposition scheme for the mechanical mixture is just a superposition of the schemes for the individual constituents.

The decomposition of photoreduced LCO proceeds in the same way as the green LCO with the formation of an intermediate carbonate finally forming crystalline $LaCoO_3$, whereas the decomposition of the mechanical mixture at $900^\circ C$ gives rise to a mixture of La_2O_3 and Co_3O_4 with traces of $LaCoO_3$.

PRASEODYMIUM TRIOXALATOCOBALTATE(III) OCTAHYDRATE (PCO) AND NEODYMIUM TRIOXALATOCOBALTATE(III) OCTAHYDRATE (NCO)

The praseodymium and neodymium compounds decompose in a similar way as the lanthanum salt. The decomposition scheme for praseodymium

salt is exactly similar to that of the lanthanum salt. There is a slight difference in the dehydration behaviour of neodymium trioxalatocobaltate(III) octahydrate. The dehydration takes place in two steps of 6.5 and 1.5 H_2O mole^{-1}. This reminds one of the step-wise dehydration behaviour of the simple neodymium oxalate decahydrate [9].

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