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PREPARATION AND THERMAL STABILITY OF TRIOXALATOCOBALTATES OF BIVALENT METALS $KM^{2+}[Co(C_2O_4)_3] \cdot x H_2O$

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ABSTRACT

Trioxalatocobaltates of bivalent metals $KM^{2+}[Co(C_2O_4)_3] \cdot x H_2O$, with M^{2+} = Ba, Sr, Ca and Pb, have been prepared, characterized and their thermal behaviour studied. The compounds decompose to yield potassium carbonate, bivalent metal carbonate or oxide and cobalt oxide as final products. The formation of the final products of decomposition is influenced by the surrounding atmosphere. Bivalent metal cobaltites of the types $KM^{2+}CoO_3$ and $M^{2+}CoO_{3-x}$ are not identified among the final products of decomposition. The study brings out the importance of the decomposition mode of the precursor in producing the desired end product.

INTRODUCTION

Potassium trioxalatometallates $K_3[M^{3+}(C_2O_4)_3] \cdot x H_2O$, where M^{3+} = Fe, Co, Ni, Mn, Al or Cr, have been known for a long time and their thermal decomposition has been studied both in solution and the solid state. There are no reports in the literature on compounds of the type $KM^{2+}[Co(C_2O_4)_3] \cdot x H_2O$. Compounds of this type with M^{2+} = Ba, Sr, Ca and Pb have been prepared, characterized and their thermal behaviour studied. We have been interested in identifying precursors which could be employed in the low-temperature chemical methods for the preparation of perovskite-type oxides. Alkaline earth cobaltites $M^{2+}CoO_{3-x}$ are generally prepared [1,2] by ceramic method by the solid state reaction between individual carbonates or oxides above 1000°C. The compounds $KM^{2+}[Co(C_2O_4)_3] \cdot x H_2O$ have been examined as possible precursors for $KM^{2+}CoO_3$ or $M^{2+}CoO_{3-x}$. The study reveals the importance of the decomposition mode of the precursors in obtaining the desired end product.

EXPERIMENTAL

Materials

All the reagents used were either BDH "Analar" or E. Merck "Pro analysi" grade.

A solution of alkaline earth salt (chloride or acetate) or lead nitrate (in the case of the lead compound) (1 M) is added slowly with stirring to an aqueous solution of potassium trioxalatocobaltate (1 M). The mixture is stirred, cooled in ice and the precipitate filtered off, washed with small portions of ice-cold water, then with acetone and air-dried. The procedure is slightly different for the calcium salt. After mixing the reagents the slight precipitate formed is filtered off and acetone is added to the filtrate to precipitate the calcium salt. The precipitate is filtered, washed with a 1 : 1 acetone—water mixture initially, and finally with acetone and air-dried. The compounds $KM^{2+}[Co(C_2O_4)_3] \cdot x\ H_2O$, with M^{2+} = Ba, Sr, Ca, Pb, have been prepared.

METHODS

The physical techniques employed such as TG, DTA, DTG, IR spectroscopy, and X-ray powder diffraction methods have been described in an earlier communication [3].

Barium and lead are estimated gravimetrically as sulphates. Calcium and strontium are estimated complexometrically by titration with EDTA at pH 12 after masking cobalt with cyanide and employing calcein and methyl thymol blue, respectively, as indicators. Cobalt is estimated volumetrically by titration with EDTA at pH 5.6 using methyl thymol blue as indicator. Potassium is estimated by flame photometry after precipitating the alkaline earths as carbonates, and lead as sulphate. Oxalate is determined by the permanganate method. Water content is determined gravimetrically by decomposing a known weight of the material and absorbing the evolved water in anhydrous magnesium perchlorate.

The procedure for analysis of the gaseous products has been described elsewhere [3].

RESULTS

The trioxalatocobaltates of bivalent metals with potassium have the general formula $KM^{2+}[Co(C_2O_4)_3] \cdot x\ H_2O$, where M^{2+} = Ba, Pb; $x = 3$ and M^{2+} = Sr, Ca; $x = 4$. The complete analytical data for these complexes are presented in Table 1. All are green in colour and are diamagnetic, having trivalent cobalt in a low-spin state. Calcium salt is highly soluble in water while the others are soluble to different extents. The IR spectra of all the compounds are remarkably similar and all the bands could be assigned by comparison with those of reported oxalato complexes [4]. All are crystalline but of low symmetry, as revealed by analysis of their X-ray powder diffraction data (Table 2).

The thermal decomposition of these compounds has been carried out in atmospheres of flowing air, carbon dioxide and a vacuum. The results indicate that the major steps of decomposition are dehydration and decomposition of the oxalate. In the case of the calcium compound, a third step of decomposition, i.e. decomposition of calcium carbonate, is also observed.

TABLE 1

Analytical data of the compounds $KM^{2+}[Co(C_2O_4)_3] \cdot x\ H_2O$

Compound	% K		% M^{2+}		% Co		% C_2O_4		% H_2O	
	Obs.	Calcd.	Obs.	Calcs.	Obs.	Calcd.	Obs.	Calcd.	Obs.	Calcd.
$KBa[Co(C_2O_4)_3] \cdot 3\ H_2O$	6.95	7.06	24.52	24.81	10.78	10.64	47.53	47.70	10.27	9.75
$KSr[Co(C_2O_4)_3] \cdot 4\ H_2O$	7.29	7.49	16.95	16.79	11.13	11.29	50.37	50.60	14.22	13.80
$KCa[Co(C_2O_4)_3] \cdot 4\ H_2O$	8.11	8.24	8.57	8.45	12.64	12.42	55.12	55.68	15.97	15.18
$KPb[Co(C_2O_4)_3] \cdot 3\ H_2O$	5.86	6.27	33.12	33.24	9.50	9.45	42.69	42.36	9.12	8.66

TABLE 2

X-Ray powder diffraction data of the compounds $KM^{2+}[Co(C_2O_4)_3] \cdot x\ H_2O$

PBCO		PSCO		PCCO		PLCO			
d(Å)	I/I_0	d(Å)	I/I_0	d(Å)	I/I_0	d(Å)	I/I_0	d(Å)	I/I_0
8.58	70	8.66	30	7.62	100	8.83	30	2.547	20
6.89	50	7.46	100	7.01	20	8.41	20	2.519	40
5.82	20	6.41	30	6.68	25	6.91	20	2.466	20
5.40	20	5.53	60	6.23	15	6.61	50	2.402	20
5.04	100	5.18	50	5.38	10	5.46	25	2.365	15
4.52	35	4.76	55	5.27	20	5.15	25	2.330	15
4.18	45	4.54	45	5.02	35	4.74	65	2.307	20
3.766	70	4.35	55	4.83	15	4.52	75	2.273	20
3.659	35	4.129	35	4.75	25	4.34	65	2.1591	10
3.490	45	3.229	20	4.59	30	4.25	75	2.1522	30
2.823	30	3.142	20	4.40	25	4.187	55	2.1347	15
		3.011	25	4.22	10	3.750	85	2.0923	30
		2.866	20	4.091	10	3.586	40	2.0473	20
		2.672	20	3.833	35	3.385	100	2.0085	15
				3.785	7	3.323	45	1.9201	10
				3.750	7	3.287	30	1.9049	10
				2.976	7	3.252	80	1.9717	10
				2.943	9	3.161	25	1.8433	10
				2.873	15	2.995	35	1.8090	20
				2.782	20	2.966	25	1.7794	35
						2.864	15	1.6850	15
						2.752	45	1.6406	10
						2.612	20	1.6299	10
						2.575	30	1.5788	15

Alkaline earth/lead cobaltites are not formed as the end products in the temperature region up to 900° C.

POTASSIUM BARIUM TRIOXALATOCOBALTATE(III) TRIHYDRATE (PBCO)

Figures 1 and 2 present the thermograms of PBCO in atmospheres of flowing air, carbon dioxide and a vacuum. Table 3 gives the temperature ranges and the corresponding weight losses for the different steps of decomposition, viz. dehydration and decomposition, of oxalates.

Dehydration of the hydrate

PBCO undergoes dehydration in the temperature range 40—200° C with a weight loss of 12—15% in different atmospheres. The observed values are very much higher than the calculated value of 9.76% for the removal of only 3 H_2O $mole^{-1}$. Gas analysis at 110° C indicates that there is evolution of carbon dioxide along with water vapour. Thus, dehydration is accompanied by partial decomposition of the oxalate. There is also a change in the colour of

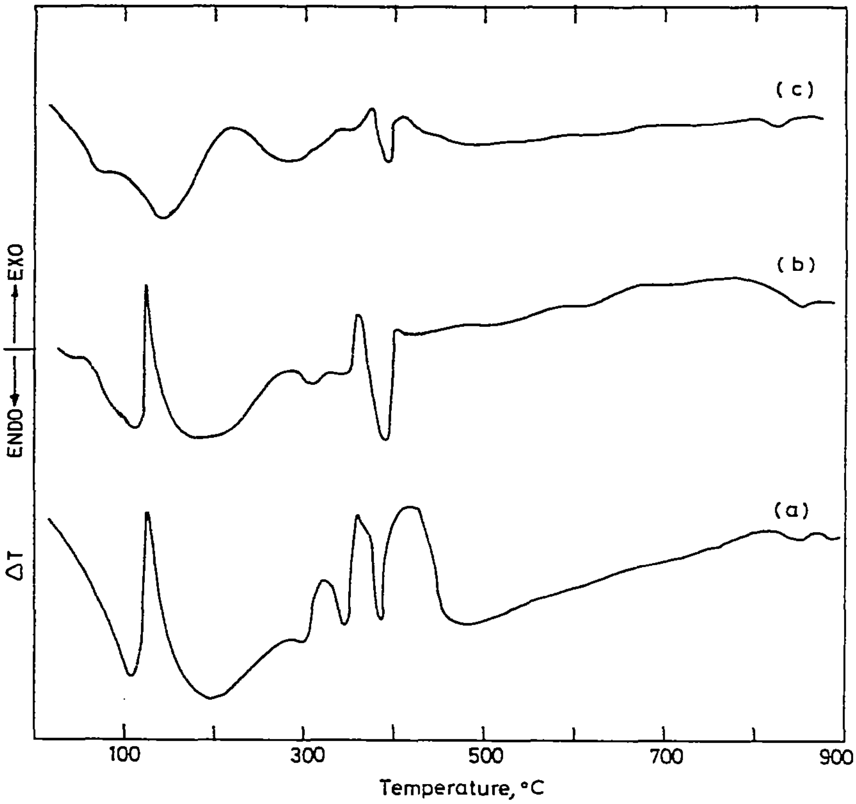

Fig. 1. DTA for PBCO in (a) air, (b) carbon dioxide, and (c) a vacuum.

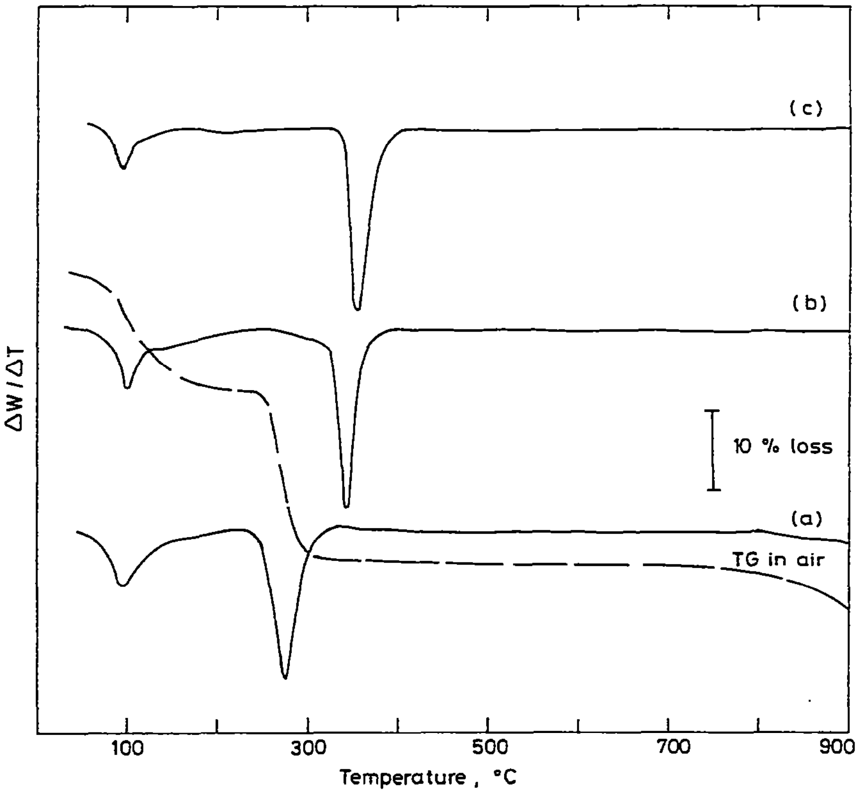

Fig. 2. DTG for PBCO in (a) air, (b) carbon dioxide, and (c) a vacuum.

TABLE 3

Temperature ranges and weight losses for the decomposition of PBCO in various atmospheres

Decomposition step	Calcd. % wt. loss	Atmosphere					
		Air		Carbon dioxide		A vacuum	
		Temp. range (°C)	% Wt. loss	Temp range (°C)	% Wt. loss	Temp. range (°C)	% Wt. loss
Partial dehydration accompanied by initial oxalate decomposition	16.08	60—175	15.0	60—200	15.0	40—200	12.0
Complete dehydration + main oxalate decomposition	21.26	225—350	21.0	300—450	23.0	300—500	28.0
Total weight loss	37.34		36.0		38.0		40.0

the compound from green to pink. The observed weight losses are comparatively lower than the calculated value of 17.71% for the removal of 3 H_2O and CO_2 mole^{-1}. Results of isothermal heating experiments at 140° C and the analysis of the gaseous products in the subsequent stage of decomposition

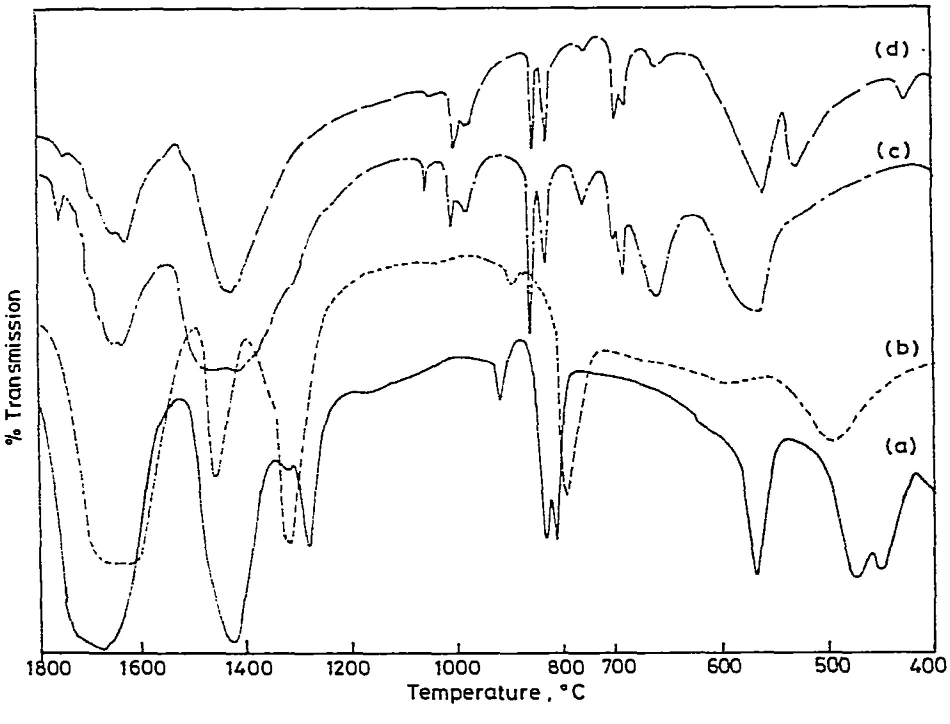

Fig. 3. IR spectra of (a) PBCO, (b) PBCO (110°C), (c) PBCO (300°C), and (d) PBCO (900°C).

reveal that dehydration is incomplete in the first stage and is irreversible. The residue is amorphous to X-rays.

Decomposition of the oxalate

The decomposition of the mixed oxalate takes place in the temperature range 200—400° C. A weight loss ranging from 21 to 28% is observed in different atmospheres. Mass spectral analysis of the gases evolved when the residue obtained at 140° C is decomposed at 300° C indicates the evolution of carbon monoxide, carbon dioxide and water vapour. The oxalate decomposition is endothermic in carbon dioxide and a vacuum, but exothermic in air due to the secondary reaction of carbon monoxide. Gas analysis indicates the CO : CO_2 ratio to be 1 : 5 instead of the expected value of 5 : 2. Thus, there is considerable disproportionation of carbon monoxide during the decomposition. The oxalate decomposition occurs at a higher temperature in carbon dioxide and a vacuum. Isothermal heating of PBCO at 300° C in air results in a weight loss of 34.89%, and the X-ray powder diffraction data of the residue indicate that potassium carbonate, barium carbonate and cobalt oxide (Co_3O_4) are the products. The IR spectrum of the residue (Fig. 3) clearly indicates the presence of ionic carbonate and a little undecomposed oxalate.

No further weight loss is observed up to 900° C as the potassium carbonate and barium carbonate formed are quite stable. However, the DTA curves show a small endotherm above 800° C which is not accompanied by any weight loss. The X-ray powder diffraction data of the residue show that the final products of decomposition in air and carbon dioxide are potassium carbonate, barium carbonate and cobalt oxide, Co_3O_4. In a vacuum, CoO is formed along with potassium and barium carbonates.

Discussion

Based on the above results, the following scheme has been proposed for the decomposition of PBCO in air

$$\mathrm{KBa[Co^{3+}(C_2O_4)_3]\cdot 3\,H_2O \xrightarrow{40-200^\circ C} [KBaCo^{2+}(C_2O_4)_{2.5}\cdot 0.5\,H_2O]^* + 2.5\,H_2O + CO_2} \tag{1}$$

$$\mathrm{[KBaCo^{2+}(C_2O_4)_{2.5}\cdot 0.5\,H_2O]^* \rightarrow 0.5\,K_2C_2O_4 + BaC_2O_4\cdot 0.5\,H_2O + CoC_2O_4} + \Delta H \tag{2}$$

$$\mathrm{0.5\,K_2C_2O_4 + BaC_2O_4\cdot 0.5\,H_2O + CoC_2O_4 + 1/6\,O_2 \xrightarrow{225-350^\circ C} 0.5\,K_2CO_3 + BaCO_3 + 1/3\,Co_3O_4 + 0.5\,H_2O + 2.5\,CO + CO_2} \tag{3}$$

Equation (1) represents the first step of decomposition which is accompanied by partial decomposition of the oxalate (gas analysis) and a reduction of trivalent cobalt to the divalent state (visible spectrum). Such an autoredox reaction has been observed for other oxalatocobaltates [5—8]. The complex [$KBaCo(C_2O_4)_{2.5} \cdot 0.5\ H_2O$] * is probably an unstable entity which splits up exothermally into a mixture of potassium, barium and cobalt oxalates. In fact, on the DTA curves, the first endothermic dehydration is accompanied by a sharp exotherm prior to the major oxalate decomposition. Moreover, the oxalate decomposition step shows greater structure on the DTA curves than that of the decomposition of a single entity. The mixed oxalates behave like the equivalent of coprecipitated products and the decomposition occurs at a lower temperature than those of the individual constituents. This oxalate decomposition results in the formation of potassium carbonate, barium carbonate and cobalt oxide (Co_3O_4) in air. No further decomposition is observed up to 900° C. There is no formation of a cobaltite either of the type $KBaCoO_3$ or $BaCoO_{3-x}$. The small endotherm observed above 800° C can be attributed to the reversible orthorhombic to hexagonal transformation of barium carbonate. In a vacuum, the Co_3O_4 formed is reduced to CoO, as revealed by the X-ray powder diffraction data of the residue. This also accounts for the excess weight loss observed in a vacuum.

POTASSIUM STRONTIUM TRIOXALATOCOBALTATE(III) TETRAHYDRATE (PSCO) AND POTASSIUM CALCIUM TRIOXALATOCOBALTATE(III) TETRAHYDRATE (PCCO)

The decomposition pattern of PSCO is similar to that of the barium salt. PSCO undergoes dehydration in three steps of 1.0 H_2O, 1.5 H_2O and 1.5 H_2O mole^{-1}, respectively, in the temperature range 40—225° C. Here also, the first dehydration step is accompanied by partial decomposition of the oxalate. The final residue of decomposition up to 900° C consists of potassium carbonate, strontium carbonate and cobalt oxides. The DTA of PSCO shows a small endotherm around 830° C, which is unaccompanied by any loss in weight. This possibly represents a phase transition of strontium carbonate.

The decomposition of PCCO, though similar to that of the barium and strontium compounds, shows an additional decomposition step beyond 600° C. The dehydration occurs in two steps of 3.5 H_2O and 0.5 H_2O mole^{-1}, respectively, in the temperature range 25—175° C. Below 600° C, the products of decomposition are potassium carbonate, calcium carbonate and cobalt oxide. In an atmosphere of flowing air or oxygen, calcium carbonate decomposes to calcium oxide and carbon dioxide, in the temperature range 600—825° C. This decomposition temperature is pushed beyond 850° C in carbon dioxide atmosphere and occurs in a considerably lower temperature range of 500—700° C in a vacuum. In carbon dioxide and a vacuum, Co_3O_4 is partially reduced to CoO.

POTASSIUM LEAD TRIOXALATOCOBALTATE(III) TRIHYDRATE (PLCO)

Like its barium and strontium analogues, PLCO decomposes through two major stages: dehydration and oxalate decomposition. Dehydration occurs in two steps. The first step of dehydration takes place in the range 50—150° C, which is also accompanied by partial oxalate decomposition; 1.5 H_2O and 1.0 CO_2 mole^{-1} are lost during this stage. Further dehydration overlaps the oxalate decomposition in the temperature range 225—500° C. Products of decomposition up to 500° C are potassium carbonate, lead oxide and cobalt oxide. The particular oxides of cobalt and lead depend on the surrounding atmosphere. In air or oxygen, Co_3O_4 and Pb_3O_4 are formed, while in a non-oxidizing atmosphere or a vacuum, CoO, PbO or Pb are formed.

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