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Note

THERMAL DECOMPOSITION OF ZINC AND CADMIUM ZIRCONYL OXALATES *

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The technological importance and special properties of XYO_3 type mixed oxides [1–8] prompted the development of chemical methods for preparing them as highly pure materials. The calcining temperature affects the properties of mixed oxide materials. The preparation of ceramic materials at low temperature results in the formation of mixed oxides in the pure homogeneous and finely divided form [9]. Oxalates are particularly useful as synthetic intermediates in the potential production of a variety of both simple and complex oxides [10]. Mixed metal oxalates have been used as precursors for the preparation of important materials such as $BaTiO_3$ [11]. Recently, thermal studies on a large number of mixed metal oxalates have been reported [9–19]. As a continuation of our previous work concerning thermal studies on zinc and cadmium titanyl oxalates [19], the present communication describes the thermal decomposition of zinc and cadmium zirconyl oxalates in dynamic atmospheres of nitrogen and oxygen.

EXPERIMENTAL

All the reagents used for the preparation of the compounds were either BDH (Poole, Great Britain), AnalaR or E. Merck (Darmstadt, G.F.R.) proanalysi grade materials. Extra pure titanium tetrachloride (Riedel-de-Haen, Hannover, G.F.R.), zirconium tetrachloride (E. Merck), zinc chloride (Aldrich, Milwaukee, WI, U.S.A.) and cadmium chloride (Aldrich) were employed.

Preparation of the compounds

Both the compounds, viz. zinc zirconyl oxalate hexahydrate and cadmium zirconyl oxalate tetrahydrate, were prepared in a similar manner. Ice-cold

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aqueous solutions of zirconium tetrachloride (0.67 mole) and zinc/cadmium chloride (0.68 mole) were mixed with stirring. This mixture was then added slowly with vigorous stirring to a hot solution of oxalic acid (1.47 mole). Excess alcohol was added to this solution, causing a bulky white precipitate to settle. The resulting solution was digested over a water bath for 30 min and kept overnight to obtain a crystalline solid product which was filtered and washed with alcohol, and then dried under vacuum over phosphorous pentoxide at room temperature.

Analyses

Carbon and hydrogen contents were determined in the usual way. To determine zinc/cadmium and zirconium, the compounds were first ignited to their oxides and the residues obtained were digested in dilute hydrochloric acid. Excess EDTA solution made by dissolving 1.5 g of reagent in 50 ml of distilled water was added to this solution and the pH of the solution was

TABLE 1

Analytical data for zinc zirconyl oxalate hexahydrate, cadmium zirconyl oxalate tetrahydrate and their intermediate products resulting in various thermal decomposition steps

Compound	Found (calcd.)%			
	C	H	Zn/Cd	Zr
$ZnZrO(C_2O_4)_2 \cdot 6\ H_2O$	10.40	2.68	14.20	19.82
	(10.51)	(2.63)	(14.32)	(19.97)
$ZnZrO(C_2O_4)_2 \cdot 4\ H_2O$	11.22	1.98	15.32	21.56
	(11.41)	(1.90)	(15.54)	(21.68)
$ZnZrO(C_2O_4)_2$	13.60		18.62	26.02
	(13.76)		(18.76)	(26.16)
$Zn_2Zr_2O_5CO_3$	2.44		29.04	40.02
	(2.64)		(28.86)	(40.25)
$ZnZrO_3$			31.80	44.41
			(31.96)	(44.58)
$CdZrO(C_2O_4)_2 \cdot 4\ H_2O$	10.38	1.82	24.62	19.98
	(10.62)	(1.77)	(24.88)	(20.19)
$CdZrO(C_2O_4)_2 \cdot 2\ H_2O$	11.54	1.02	26.92	22.08
	(11.28)	(0.96)	(27.04)	(21.94)
$CdZrO(C_2O_4)_2$	12.42		29.40	24.23
	(12.60)		(29.61)	(24.03)
$Cd_2Zr_2O_4(C_2O_4)CO_3$	5.60		36.12	29.28
	(5.81)		(36.30)	(29.46)
$Cd_2Zr_2O_5CO_3$	2.08		41.27	33.25
	(2.19)		(41.08)	(33.34)
$CdZrO_3$			44.52	36.18
			(44.67)	(36.25)

adjusted to ~4.0 with dilute ammonium hydroxide. From this solution zinc was estimated as zinc ammonium phosphate and cadmium as cadmium molybdate [20]. After the precipitation of zinc/cadmium, the zirconium was determined from the filtrate by precipitation with 1% aqueous cupferron solution in strongly acidic medium. The precipitate was ignited to 1273 K and weighed as ZrO_2 [20]. The analytical data for the compounds and the intermediates obtained in various thermal decomposition steps are given in Table 1.

Physical measurements

IR spectra of the compounds were recorded in the range 4000–200 cm^{-1} with a Perkin-Elmer 621 grating spectrophotometer. Thermogravimetric (TG) and derivative thermogravimetric (DTG) curves were recorded simultaneously on a SETARAM (Lyon, France) G-70 thermoanalyzer with a sample size of ~30 mg, a heating rate of 8 K min^{-1} and a gas flow rate of 10 ml min^{-1}. The DSC curves were recorded on a Perkin-Elmer, Model DSC-1 differential scanning calorimeter in the temperature range 273–773 K in an atmosphere of nitrogen. About 10 mg of sample were used. The intermediate compounds obtained in the various thermal decomposition steps were identified by elemental analyses and IR spectral studies.

RESULTS AND DISCUSSION

Figures 1 and 2 show the thermogravimetric and derivative thermogravimetric curves of zinc zirconyl oxalate hexahydrate and cadmium zirconyl oxalate tetrahydrate, respectively, in dynamic atmospheres of nitrogen and oxygen. Figure 3 incorporates the DSC curves of CZO in nitrogen only.

It is evident from the thermogravimetric curves that the thermal decomposition of both the compounds proceeds through three major steps, viz. (i) dehydration of the hydrated oxalate, (ii) decomposition of the oxalate to the intermediate carbonate, and (iii) decomposition of the intermediate carbonate to the oxide.

Dehydration

Dehydration of both the compounds, viz. ZZO and CZO, takes place in two stages. In the case of ZZO first stage occurs between 313 and 353 K and the second stage between 353 and 413 K. The observed weight loss for the first and second stage dehydration corresponds to the loss of 2 and 4 moles of water, respectively, per mole of ZZO, which indicates that the parent compound under investigation was hexahydrated.

CZO becomes dehydrated between 323 and 413 K and 413 and 513 K.

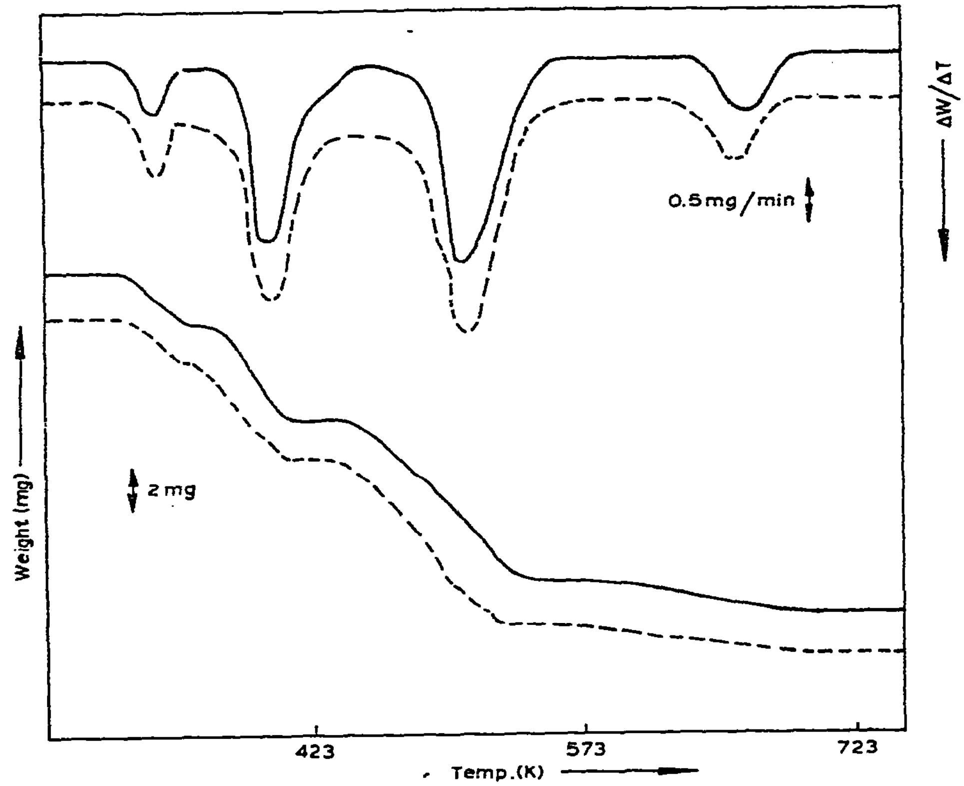

Fig. 1. TG and DTG curves of ZZO in N_2 (————) and O_2 (- - - - - -).

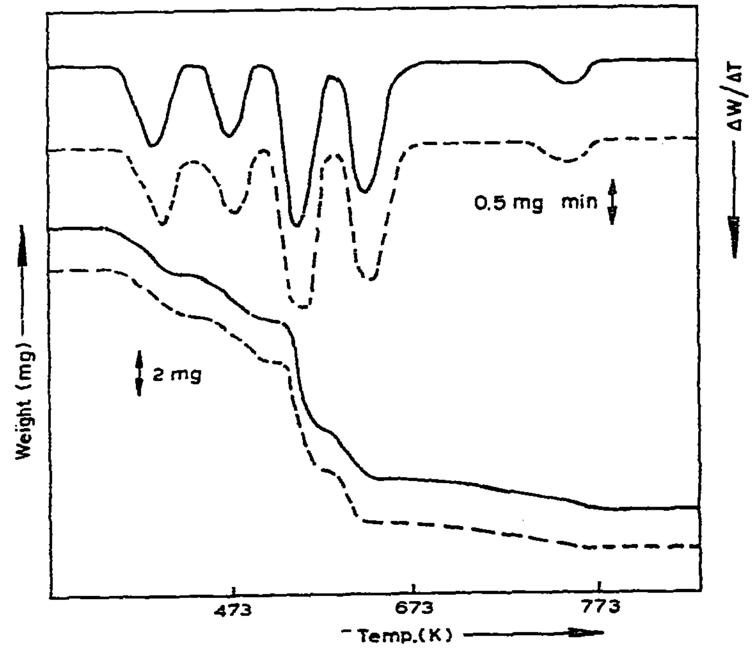

Fig. 2. TG and DTG curves of CZO in N_2 (————) and O_2 (- - - - - -).

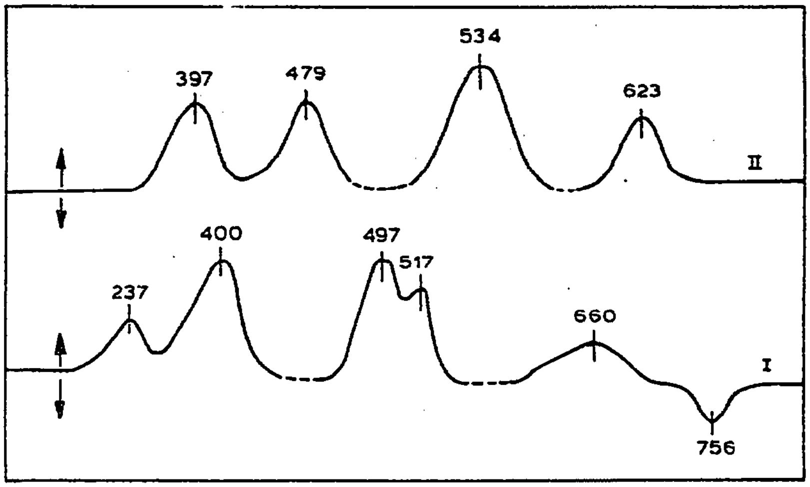

Fig. 3. DSC curves of ZZO (I) and CZO (II) in N_2.

The observed weight loss for both first and second stage decomposition corresponds to the loss of 2 moles of water, showing that the initial compound contained 4 moles of water per mole of CZO.

The expected endothermic behaviour for the dehydration process associated with these compounds was observed from DSC curves in approximately the same temperature ranges.

Decomposition of the oxalate

As soon as dehydration of the compound is complete, decomposition of the oxalate starts. Decomposition of dehydrated ZZO to the respective carbonate takes places in a single endothermic step. The DSC curves corresponding to this step show a small doublet which may be due to nonequivalence of oxalate groups, while in the case of CZO two consecutive steps are observed. In the first step the oxalate groups partly decompose to the carbonate, resulting in the formation of an oxalato-carbonate complex, which further decomposes in the second step to give the respective carbonate. The residue obtained after the first endothermic decomposition step of anhydrous CZO has been assigned the composition $Cd_2Zr_2O_4(C_2O_4)CO_3$ on the basis of its elemental analyses and IR spectral studies. The IR spectra of this residue showed the bands corresponding to oxalate as well as carbonate vibrations. The principal band of the oxalato group is at ~ 1650 cm^{-1} and that of the carbonate at ~ 1320 cm^{-1}. Further decomposition of this intermediate which is also endothermic results in the formation of the pure carbonate, $Cd_2Zr_2O_5CO_3$. The residue can be isolated by isothermal heating of CZO at 640 K for 24 h.

Decomposition of the carbonate

Decomposition of the carbonates, $Zn_2Zr_2O_5CO_3$ and $Cd_2Zr_2O_5CO_3$, to the corresponding metal zirconates, $ZnZrO_3$ and $CdZrO_3$, takes place in a single step. The DSC curves corresponding to this step were obtained only in the case of ZZO due to the limited temperature range of the instrument (273–773 K). The DSC curves indicate that the initial decomposition of $Zn_2Zr_2O_5CO_3$ is endothermic, followed by an exothermic reaction. This exothermic behaviour of the DSC curves is probably due to the transition of one crystalline form of zinc zirconate to another because for this exotherm, TG and DTG do not correspond to any weight change. The difference in the peak temperatures of DSC and DTG curves may be attributed to two factors: the difference in the design of the two furnaces, and the difference in the flow rate of the gas.

On the basis of the above results the following tentative decomposition schemes may be proposed for the decomposition of ZZO and CZO.

TABLE 2

Temperature range and % weight loss for different decomposition steps of zinc zirconyl oxalate hexahydrate (ZZO) and cadmium zirconyl oxalate tetrahydrate (CZO)

Decomposition steps	In N_2		In O_2		Calcd. % wt. loss
	Temp. range (K)	% wt. loss	Temp. range (K)	% Wt. loss	
Decomposition of ZZO					
1. Dehydration; first stage	313–353	8.08	313–353	7.81	7.88
second stage	353–413	16.06	353–413	16.12	15.77
2. Decomposition of oxalate	433–548	26.45	433–530	26.78	26.72
3. Decomposition of carbonate	573–713	4.98	563–713	4.98	4.82
Total % wt. loss		55.57		55.69	55.19
Decomposition of CZO					
1. Dehydration; first stage	323–413	7.70	323–423	7.81	7.70
second stage	413–513	7.66	413–513	7.58	7.70
2. Decomposition of oxalate; first stage	523–573	17.98	423–568	17.83	18.39
second stage	573–623	8.02	573–613	8.23	7.70
3. Decomposition of carbonate	653–888	4.66	650–875	4.82	4.70
Total % wt. loss		46.02		46.27	46.19

Decomposition of ZZO

$ZnZrO(C_2O_4)_2 \cdot 6\,H_2O \rightarrow ZnZrO(C_2O_4)_2 \cdot 4\,H_2O + 2\,H_2O$

$ZnZrO(C_2O_4)_2 \cdot 4\,H_2O \rightarrow ZnZrO(C_2O_4)_2 + 4\,H_2O$

$2\,ZnZrO(C_2O_4)_2 \rightarrow Zn_2Zr_2O_5CO_3 + 4\,CO + 3\,CO_2$

$Zn_2Zr_2O_5CO_3 \rightarrow 2\,ZnZrO_3 + CO_2$

Decomposition of CZO

$CdZrO(C_2O_4)_2 \cdot 4\,H_2O \rightarrow CdZrO(C_2O_4)_2 \cdot 2\,H_2O + 2\,H_2O$

$CdZrO(C_2O_4)_2 \cdot 2\,H_2O \rightarrow CdZrO(C_2O_4)_2 + 2\,H_2O$

$2\,CdZrO(C_2O_4)_2 \rightarrow Cd_2Zr_2O_4(C_2O_4)CO_3 + 3\,CO + 2\,CO_2$

$Cd_2Zr_2O_4(C_2O_4)CO_3 \rightarrow Cd_2Zr_2O_5CO_3 + CO + CO_2$

$Cd_2Zr_2O_5CO_3 \rightarrow 2\,CdZrO_3 + CO_2$

The temperature range and mass loss for various decomposition steps of ZZO and CZO in atmospheres of nitrogen and oxygen are listed in Table 2.

REFERENCES

1 J.K. Hulm, Phys. Rev., 92 (1953) 504.
2 G.R. Fonda, J. Opt. Soc. Am., 47 (1957) 877.
3 F.P. Gangliano, R.M. Lumley and L.S. Watkins, Proc. IEEE, 57 (1961) 114.
4 L.F. Johnson, G.D. Boyd, K. Nassau and R.R. Soden, Phys. Rev., 126 (1962) 1406.
5 E.C. Subba Rao, J. Phys. Chem. Solids, 23 (1962) 655.
6 J.W. Gilliland and M.S. Hall, Electrochim. Technol., 4 (1966) 378.
7 F.S. Chem, Proc. IEEE, 58 (1970) 1440.
8 G.H. Heartling and C.E. Land, J. Am. Ceram. Soc., 54 (1971) 1.
9 W.S. Clabaugh, E.M. Swiggard and R. Gilchrist, J. Res. Natl. Bur. Stand., 56 (1956) 289.
10 B.V. Strizhakov, A.V. Lapitskii, L.G. Vlasov and A.V. Travertrav, Dokl. Akad. Nauk S.S.S.R., 133 (1960) 1347.
11 O. Saburi, Ceram. Abstr., (1962) 202j.
12 P.K. Gallagher and T. Schrey, J. Am. Ceram. Soc., 46 (1963) 567.
13 P.K. Gallagher and J. Thompson, Jr., J. Am. Ceram. Soc., 48 (1965) 644.
14 A. Aykan, J. Am. Ceram. Soc., 51 (1968) 577.
15 A.P. Sheinkman, N.V. Yunusova, V.P. Oschev and A.A. Kondrashenkov, Russ. J. Inorg. Chem., 19 (1974) 206.
16 H.S. Gopalkrishna Murthy, M. Subba Rao and T.R. Narayana Kutty, J. Inorg. Nucl. Chem., 37 (1975) 891; 37 (1975) 1875; 38 (1975) 596; 38 (1976) 417; Thermochim. Acta, 13 (1975) 183.
17 T. Gangadevi, M. Subba Rao and T.R. Narayanan Kutty, Indian J. Chem., 19A (1980) 303.
18 A.K. Sharma, S. Kumar and N.K. Kaushik, Thermochim. Acta, 47 (1981) 149; J. Anal. Appl. Pyrolysis, 3 (1982) 271.
19 A.K. Sharma and N.K. Kaushik, Thermochim. Acta, 49 (1981) 385.
20 A.I. Vogel, A Textbook of Quantitative Inorganic Analyses, Longmans Green, London, 3rd edn., 1964.