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Note

THERMAL STUDIES ON ZINC AND CADMIUM TITANYL OXALATES

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The technical importance of mixed oxides [1—7], due to the possession of desirable dielectric and piezoelectric properties, prompted the development of chemical methods for the preparation of these compounds as highly pure materials. Mixed metal oxalates act as important synthetic precursors for mixed oxides. In recent years, the thermal decomposition of a large number of bivalent metal titanyl oxalates has been studied [8—12]. At higher temperatures, these compounds yield the corresponding metal titanates, the compounds of technical interest. However, in the literature there is no mention of the zinc and cadmium titanyl oxalates. The present communication describes the preparation, characterization and thermal investigation of zinc and cadmium titanyl oxalates.

EXPERIMENTAL

All the reagents used for the preparation of these compounds were either E. Merck or BDH (Analar).

Preparation of the compounds

Both the compounds, viz. ZTO and CTO, were prepared in a similar manner. Aqueous solutions of titanium tetrachloride (0.67 mole) and zinc/cadmium chloride (0.68 mole) were mixed with stirring. This mixture was then added slowly with continuous stirring to a hot aqueous solution of oxalic acid (1.47 mole). Excess alcohol was added to the above solution until the bulky white precipitate settled down. The resulting solution was kept overnight. The product was then filtered and washed with alcohol, and then dried in vacuum over P_4O_{10} at room temperature. The analytical results (%), with the calculated figures in parentheses, were: for ZTO, C 12.5(12.7), H 2.2(2.1), Zn 17.2(17.3), Ti 12.5(12.7); and for CTO, C 11.0(11.3), H 2.0-(1.9), Cd 26.2(26.5), Ti 11.2(11.3).

Physical measurements

IR spectra of these compounds were recorded in KBr medium in the region 4000—200 cm^{-1} with a Perkin-Elmer-621 grating spectrophotometer.

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TG and DTG were recorded simultaneously on a SETARAM G-70 thermoanalyzer (Lyon, France) with a sample size of 30—40 mg, a heating rate of 8 K min^{-1} and a gas flow rate of 10 ml min^{-1}. The DSC curves were recorded using a Perkin-Elmer differential scanning calorimeter Model DSC-1 in the temperature range 273—773 K, with a sample size of 10 mg and a heating rate of 8 K min^{-1}.

RESULTS AND DISCUSSION

Both the compounds were isolated in white crystalline form. Satisfactory elemental analysis and IR spectra confirm that the method used for the preparation and isolation of these compounds yields materials of high purity.

IR spectra

The IR spectra of these compounds have been discussed on the basis of empirical band assignment for the free oxalate anion [13]. The bands occurring around 3350(vs), 1620(s), 1420(m), 1350(m), 910(m), 800(s), 525(w), 500(w) and 400(w) cm^{-1} may be assigned to $\nu(\text{OH})$ $\nu_{as}(\text{C=O})$, $\nu(\text{C—O}) + \nu(\text{C—C})$, $\nu(\text{C—O}) + \delta(\text{O—C=O})$, $\nu(\text{C—O}) + \delta(\text{O—C=O}) + \nu(\text{Ti—O})$, $\delta(\text{O—C=O}) + \nu(\text{Ti—O})$, $\nu(\text{Ti—O}) + \nu(\text{C—C})$, ring deformation + $\delta(\text{O—C=O})$ and $\nu(\text{Ti—O})$ + ring deformation, respectively [14].

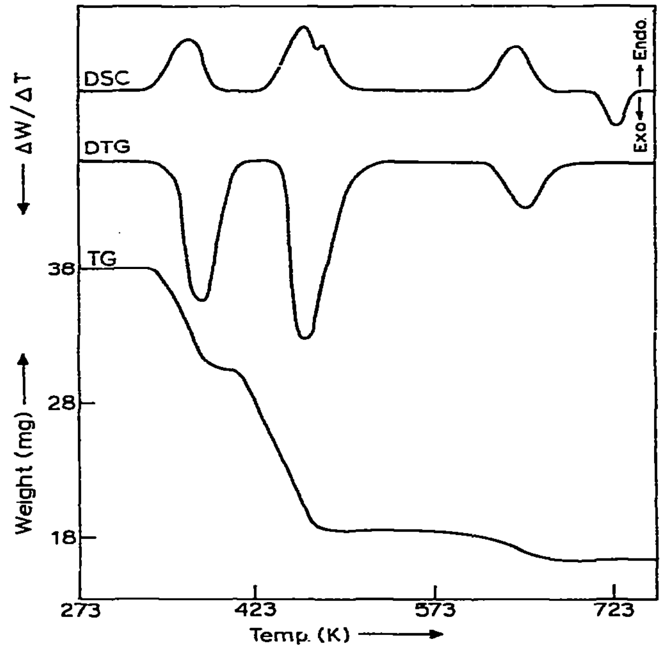

Fig. 1. TG, DTG and DSC curves of ZTO in nitrogen.

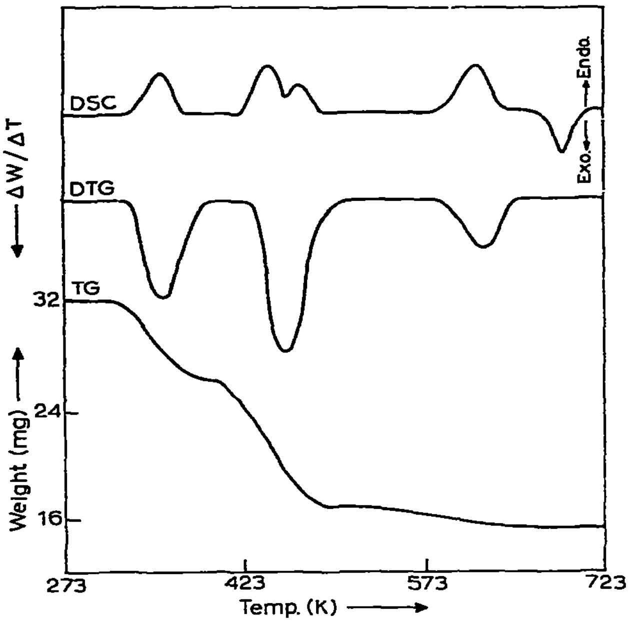

Fig. 2. TG, DTG and DSC curves of CTO in nitrogen.

Thermal analysis

Figures 1 and 2 present the TG, DTG and DSC curves of ZTO and CTO, respectively in a static nitrogen atmosphere. It is evident from the TG and DTG curves that the thermal decomposition of ZTO and CTO proceeds through three major steps, viz. dehydration of the hydrated oxalate, decomposition of the oxalate to the carbonate, and finally decomposition of the carbonate to the respective metal titanate.

Dehydration

ZTO and CTO become dehydrated in a single step. The dehydration of ZTO occurs in the temperature range 333—383 K while that of CTO takes place between 320 and 383 K. The expected endothermic behaviour for the dehydration process associated with these compounds has been observed from DSC curves in the same temperature range. The observed weight loss for the first stage of decomposition of both ZTO and CTO corresponds to the four water molecules present in these compounds.

Decomposition of the oxalate

Decomposition of the anhydrous oxalate to the corresponding carbonate starts immediately after dehydration. The decomposition of anhydrous ZTO is observed in the temperature range 393—475 K, while that of anhydrous CTO occurs between 393 and 483 K. In this step 2 moles of the anhydrous oxalate lose 3 moles of CO_2 and 4 moles of CO to give the corresponding carbonate. The DSC curves corresponding to this step show doublets (endotherms) which may be due to non-equivalence of the oxalate groups.

Decomposition of the carbonate

Decomposition of the carbonates of ZTO and CTO occur between 580 and 683 K and 513 and 735 K, respectively, 1 mole of CO_2 being lost to give the corresponding metal titanate. The DSC curves corresponding to this step show that the initial reaction is endothermic, followed by an exothermic reaction. The exothermic reaction is probably due to the transition of one crystalline form of the metal titanate to another. TG and DTG curves do not show any weight change for this temperature interval.

The difference in the peak temperatures of DTG and DSC 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 thermal decomposition of ZTO and CTO.

Decomposition of ZTO

$$ZnTiO(C_2O_4)_2 \cdot 4\,H_2O \xrightarrow{333-383\,K} ZnTiO(C_2O_4)_2 + 4\,H_2O$$

$$2\,ZnTiO(C_2O_4)_2 \xrightarrow{393-475\,K} Zn_2Ti_2O_5CO_3 + 4\,CO + 3\,CO_2$$

$$Zn_2Ti_2O_5CO_3 \xrightarrow{580-683\,K} 2\,ZnTiO_3 + CO_2$$

Decomposition of CTO

$$CdTiO(C_2O_4)_2 \cdot 4\,H_2O \xrightarrow{320-383\,K} CdTiO(C_2O_4)_2 + 4\,H_2O$$

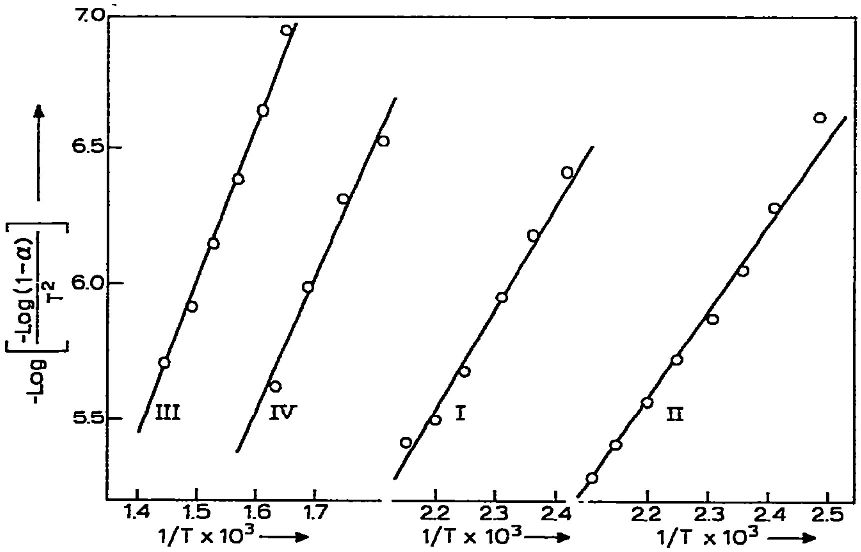

Fig. 3. Coats and Redfern's linearization curves for second (I, II) and third step (III, IV) decomposition reactions of ZTO and CTO, respectively, in nitrogen.

TABLE 1

Temperature range, weight loss, activation energy and order of reaction for different decomposition steps of ZTO and CTO

Decomposition step	Temp. range (K)	% Wt. loss		Activation energy (kcal mole^{-1})	Order of reaction, *n*
		Obs.	Calcd.		
Decomposition of ZTO					
(1) Dehydration	333—383	18.88	19.08		
(2) Decomposition of oxalate	393—475	32.53	32.34	17.32	1
(3) Decomposition of carbonate	580—683	5.98	5.83	27.24	1
		57.39	57.25		
Decomposition of CTO					
(1) Dehydration	320—383	17.14	16.97		
(2) Decomposition of oxalate	393—483	29.02	28.75	14.13	1
(3) Decomposition of carbonate	513—735	5.04	5.19	22.80	1
		51.20	50.91		

$$2\ \mathrm{CdTiO(C_2O_4)_2} \xrightarrow{393\text{—}483\,\mathrm{K}} \mathrm{Cd_2Ti_2O_5CO_3} + 4\ \mathrm{CO} + 3\ \mathrm{CO_2}$$

$$\mathrm{Cd_2Ti_2O_5CO_3} \xrightarrow{513\text{—}735\,\mathrm{K}} 2\ \mathrm{CdTiO_3} + \mathrm{CO_2}$$

Calculation of the apparent activation energy and order of reaction has been performed for the second and third step thermal decomposition reactions in nitrogen atmosphere employing the graphical method of Coats and Redfern [15]. The plot of $\{-\log[-\log(1-\alpha)/T^2]\}$ vs. $1/T \times 10^3$ for $n = 1$ (where n = apparent order of reaction) gives a straight line (Fig. 3) with slope $-E/2.303R$. The thermal stability data, mass loss, apparent activation energy and order of reaction for different decomposition steps are listed in Table 1.

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