INFRARED AND THERMAL STUDIES OF STRONTIUM ZIRCONYL OXALATE HEXAHYDRATE

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ABSTRACT

Strontium zirconyl oxalate hexahydrate (SZO) is prepared and characterized by chemical analysis and IR spectral studies. Its thermal decomposition studies have been made using thermogravimetry (TG) and differential thermal analysis (DTA). The decomposition has been found to proceed through three major steps (i) a three stage dehydration, (ii) decomposition of the oxalate and (iii) decomposition of carbonate to strontium zirconate. Carbon dioxide is found to be trapped in the solid during the decomposition of the oxalate. The identification of residues at various stages has been done by IR spectra and chemical analysis.

INTRODUCTION

In continuation of our investigation on the thermal decomposition of zirconyl oxalates of alkaline earth metals[1], preparation, characterization and thermal decomposition of strontium zirconyl oxalate hexahydrate (SZO) is described. The end product has been found to be strontium zirconate. Strontium zirconate can also be prepared by calcining the strontium carbonate and zirconium dioxide mixture at a higher temperature $(1300\,^\circ C)$[2] but the yield was poor. This paper deals with an attempt to prepare strontium zirconate in higher yield by a relatively simpler method from strontium zirconyl oxalate hexahydrate.

The thermal decomposition of titanyl oxalates of alkaline earths[3–7], uranyl and plutonyl oxalates of barium[8] have been reported in the literature but no such information is available regarding the preparation and thermal decomposition of SZO. Hence, the present system has been undertaken to study the mode of thermal decomposition of strontium zirconyl oxalate hexahydrate. A tentative scheme for the multistage decomposition of SZO has been proposed. Thermogravimetry, isothermal studies and chemical analyses enable us to arrive at our conclusions which in turn are supported by IR spectra.

EXPERIMENTAL

All the reagents used in the present work were of BDH analar quality. The

zirconium oxychloride octahydrate was from Fluka AG. Buchs SG, Switzerland and was recrystallised twice before use. The IR spectrum of the recrystallised compound compared well with its spectrum given in the literature[9].

Strontium zirconyl oxalate hexahydrate was prepared by the procedure described earlier for the preparation of (BZO)[1], using strontium chloride in the place of barium chloride. The product was washed with acetone and air dried.

Strontium in the complex was determined as sulphate after destroying the oxalate. Zirconium was determined as dioxide after complexing as tetramandetate and then destroying it. The oxalate was determined by permanganimetry. Water content was determined by heating a known amount of sample and absorbing the evolved water in anhydrous magnesium perchlorate. The chemical analysis of the acetone washed SZO is Sr 18.10, ZrO 22.5, C_2O_4 37.0, H_2O 22.6% whereas that calculated for $SrZrO(C_2O_4)_2 6H_2O$ (SZO) is Sr 18.30, ZrO 22.40, C_2O_4 36.76, H_2O 22.56%.

Thermogravimetry was carried out using a Stanton Redcroft TG-770 thermo balance fitted with temperature programmer and recorder "Servoscribe 2s", and differential thermal analysis by a Fisher differential thermalyzer, model 260 P fitted with an automatic voltage stabiliser, recorder and amplifier. 5–10 mg samples were taken in platinum crucibles for thermogravimetry and the heating rate was 10°C min^{-1}. 150–200 mg samples were taken for DTA in quartz crucibles using calcined α-alumina as reference material and the heating rate was 10°C min^{-1}. IR spectra were recorded on a Beckman IR-20 in the range of 250–4000 cm^{-1} with samples in KBr pellets. X-rays were taken on a Seimens X-ray diffractometer using CoK-α radiation. The X-ray pattern of SZO indicates that it is a crystalline compound. Some of the 2θ and d-values are reported in Table 1.

TABLE 1

X-RAY DATA OF SZO

2θ	d-Values[a] (Å)
23.4	4.09 (s)
26.8	3.86 (m)
27.5	3.76 (s)
29.6	3.50 (s)
30.1	3.44 (v.s)
36.8	2.83 (st)
48.3	2.18 (m)
51.4	2.06 (m)
52.8	2.01 (m)
56.6	1.88 (m)

[a] s = small, st = strong, m = medium, v.s = very small.

RESULTS AND DISCUSSION

Figure 1 gives the TG, DTG and DTA curves in air. It reveals that all the thermal effects are accompanied by weight losses. There are three major steps in the decomposition of SZO. These being (i) the dehydration, (ii) the decomposition of the oxalate to a carbonate and (iii) the decomposition of the carbonate to strontium metazirconate, $SrZrO_3$. The temperature ranges and the observed weight losses for the decomposition of SZO are given in Table 2. The different stages of the thermal decomposition of SZO will now be discussed.

Dehydration of the hexahydrate

Dehydration of SZO takes place between 25°–250 °C in three stages which are shown in the thermogram (Fig. 1). The third stage of dehydration, though clearly
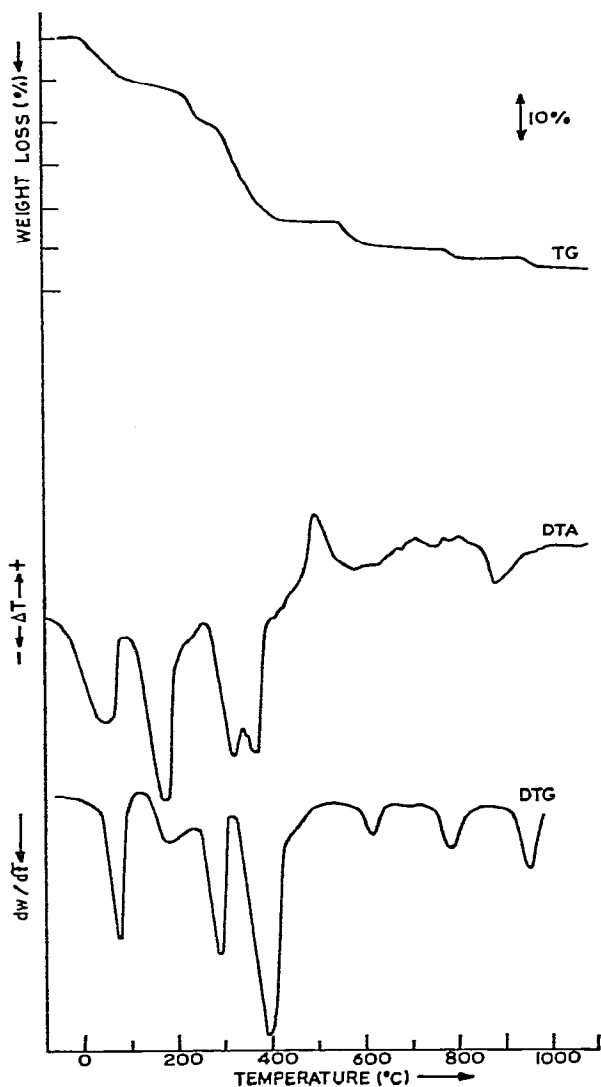
Fig. 1. TG, DTA and DTG of SZO in air.

TABLE 2

TG DATA OF SZO

Decomposition step	Temp. range (°C)	Calc. wt. loss (%)	Obsd. wt. loss (%)
1st step dehydration	25–190	11.27	10.40
Dehydration of SZO	190–325	11.27	10.50
Decompn. of oxalate	325–475	17.91	18.19
Evolution of carbon dioxide	475–650	7.75	8.50
Partial decompn. of carbonate	650–830	2.25	1.59
Final decompn. of carbonate	830–1000	2.38	3.30

visible in the DTA curve, is combined in TG with the oxalate decomposition. Chemical analysis of the sample obtained in isothermal experiments at 200°C shows that both the oxalate groups are intact. On the other hand, the samples heated at 250°C for 2 hrs reveal that some of the oxalate is decomposed. This fact supports the overlap of dehydration and oxalate decomposition peaks in the DTA trace. The observed weight loss for dehydration of SZO is 10.50% against the calculated value of 11.27% for $6H_2O$ per mole of SZO.

Oxalate decomposition

The decomposition of the oxalate as such is a multistep process in the range 325°–475°C. From the DTA curve it is evident that even before the dehydration is complete the oxalate decomposition starts. This stage appears clearly in DTG. The observed weight loss at this stage is 18.20% whereas the calculated value is 18.0%. The sample obtained from isothermal experiments at 450° shows that no oxalate is present. The IR spectra of this residue contains a band at 2310 cm^{-1} in addition to the carbonate bands. This band at 2310 cm^{-1} may be due to trapped carbon dioxide present in the solid. This stage involves a complex set of reactions which are probably the decomposition of oxalate, oxidation and/or disproportionation of carbon monoxide and the oxidation of the carbon produced during the disproportionation. The DTA curve (Fig. 1) shows an endothermic peak around 330°C followed by an exothermic peak around 500°C. The latter peak may be due to the oxidation of evolved carbon monoxide.

Decomposition of carbonate

Weight loss between 475°–650°C corresponds to the evolution of trapped carbon dioxide that was present in the residue in the (eqn. 2a) stage. The percentage weight loss from TG is 8.50 against the calculated value of 7.75. This stage clearly appeared in DTG (Fig. 1) but does not show up in DTA (Fig. 1). The next weight loss occurs between 650°–830°C which corresponds to the loss of half a mole of carbon dioxide. The percentage weight loss is 1.59 against the calculated value of 2.2.

This stage (eqn. 2b) clearly appears in DTG and TG but not in DTA. This may be due to a large baseline shift and the small amount of reaction that is involved. Final decomposition of the remaining carbonate occurs between 830°–1000°. The weight loss at this last stage is 3.30% whereas the calculated weight loss is 2.38%.

Figure 2 gives the IR spectra of various materials. The spectrum (A) shows the principal band v_{as} (C–O) of strontium zirconyl oxalate at 1660 cm^{-1}. Other bands which are all combination bands may be assigned to different normal modes of vibration of oxalate group[10]. The IR spectra of samples heated at 190°C and 250°C respectively show all the bands assigned to oxalate. Spectrum (B) reveals a new band at 2310 cm^{-1} which may be due to the presence of trapped carbon dioxide. The lower value of the fundamental frequency for CO_2 is probably due to some interaction of this gas with the lattice. The remaining bands are assigned to the ionic carbonate[11], the v_{as} at 1450 cm^{-1} is almost symmetrical and v_s at 1060 cm^{-1} is weakly active. The deformation bending occurs at 850 cm^{-1} and is sharp. Spectrum (C) of a sample heated at 920°C indicates the formation of strontium zirconate containing small amount of carbonate impurity[12]. However in the sample heated at the same temperature for several hours no carbonate impurity was observed.
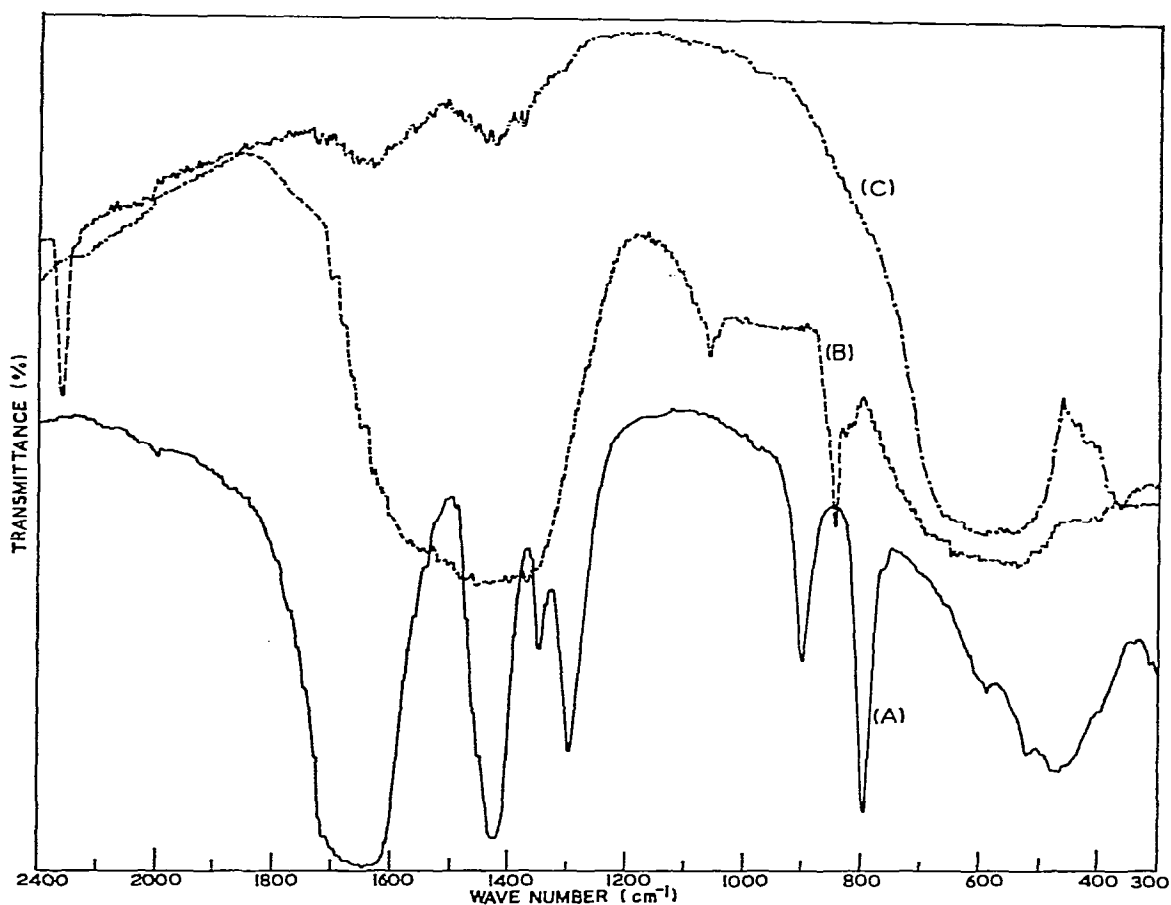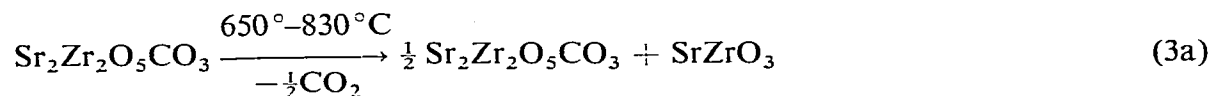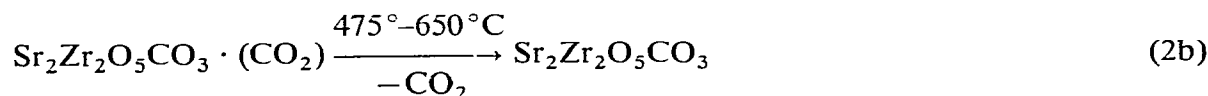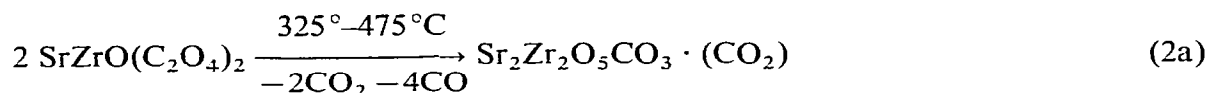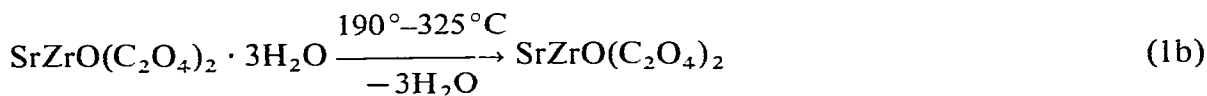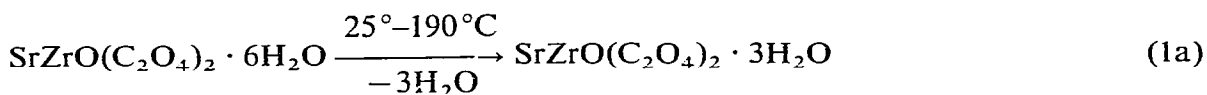

Fig. 2. IR spectra of (A) BZO, (B) BZO heated at 450°C and (C) BZO heated at 920°C.

All the above observations allow us to propose a tentative (major) three stage scheme for the thermal decomposition of strontium zirconyl oxalate hexahydrate (SZO) which is as follows:

$$SrZrO(C_2O_4)_2 \cdot 6H_2O \xrightarrow[-3H_2O]{25°-190°C} SrZrO(C_2O_4)_2 \cdot 3H_2O \qquad (1a)$$

$$SrZrO(C_2O_4)_2 \cdot 3H_2O \xrightarrow[-3H_2O]{190°-325°C} SrZrO(C_2O_4)_2 \qquad (1b)$$

$$2\,SrZrO(C_2O_4)_2 \xrightarrow[-2CO_2\,-4CO]{325°-475°C} Sr_2Zr_2O_5CO_3 \cdot (CO_2) \qquad (2a)$$

$$Sr_2Zr_2O_5CO_3 \cdot (CO_2) \xrightarrow[-CO_2]{475°-650°C} Sr_2Zr_2O_5CO_3 \qquad (2b)$$

$$Sr_2Zr_2O_5CO_3 \xrightarrow[-\frac{1}{2}CO_2]{650°-830°C} \tfrac{1}{2}\,Sr_2Zr_2O_5CO_3 + SrZrO_3 \qquad (3a)$$

$$\tfrac{1}{2}\,Sr_2Zr_2O_5CO_3 \xrightarrow[-\frac{1}{2}CO_2]{830°-1000°C} SrZrO_3 \qquad (3b)$$

Equation (1) represents the dehydration of SZO in three stages as is shown in DTA and DTG traces. The part of the water that is given off below 100°C indicates that it is loosely bound water. Stage (1b) represents the complete dehydration of SZO. Equation (2) comprises two stages again: a) corresponds to the loss of four moles of carbon monoxide and two moles of carbon dioxide per two moles of anhydrous strontium zirconyl oxalate, b) involves the evolution of carbon dioxide that was present somehow in the lattice. The residue obtained in both stages (2a and 2b) gave effervescence when treated with mineral acids indicating the presence of carbonate. In eqn. (3) again there are two steps: (a) the partial decomposition of the carbonate and (b) the final carbonate decomposition. In each step $\frac{1}{2}$ mole of CO_2 is lost and finally strontium metazirconate ($SrZrO_3$) is obtained.

From the above discussions it is clear that the weight loss steps in thermogravimetry and the explanations based on them are very limited in scope and the intermediates often may not represent stable compositions. The composition of the residues obtained in the isothermal experiments need not and often do not tally with the apparent composition assigned by weight loss measurements in thermo gravimetry.

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