Thermochimica Acta, 31 (1979) 31–37

PREPARATION, CHARACTERISATION AND THERMAL DECOMPOSITION OF BARIUM ZIRCONYL OXALATE

V. B. REDDY AND P. N. MEHROTRA
Department of Chemistry, Roorkee University, Roorkee-247 672 (India)
(Received 22 May 1978)

ABSTRACT

Barium zirconyl oxalate hydrate (BZO) is prepared and characterised by chemical analysis and IR spectral studies. Thermal decomposition studies have been made using TG and DTA techniques. The decomposition has been found to proceed through four steps. The first step involves a two-stage dehydration (100–190°C, 190–260°C) and the second step the decomposition of oxalate (260–460°C). The third step involves the evolution of carbon monoxide present in the lattice and partial decomposition of carbonate. The fourth step involves the final stage decomposition of carbonate (760–920°C) giving barium zirconate as an end product. The identification of compounds at various stages has been done by IR spectra. The X-ray diffraction pattern of BZO confirms that it is a crystalline compound.

INTRODUCTION

The importance of the zirconates of a number of bivalent metals in various fields of technology prompted us to prepare and investigate the thermal decomposition of barium zirconyl oxalate hydrate (BZO), where the endproduct has been found to be barium zirconate. Barium zirconate can also be prepared by calcining a barium carbonate and zirconium dioxide mixture at a higher temperature (1100°C)[1]. Our method of preparation of barium zirconate by thermal decomposition of BZO involves higher yield, is simpler and hence attracts special interest.

The thermal decomposition of titanyl oxalates of Ba, Ca, Sr and Pb has been reported in the literature[2–5] but no such information is available regarding the thermal decomposition of zirconyl oxalates. Hence, the thermal decomposition of BZO has been undertaken and a tentative scheme for the multi-stage decomposition has been proposed. The thermogravimetric analysis and isothermal studies enable us to arrive at conclusions which are supported by IR spectra.

EXPERIMENTAL

All the reagents used in the present work were of BDH AnalaR quality. The zirconium oxychloride octahydrate was of Fluka AG (Buchs SC, Switzerland) and was recrystallised twice before use. The IR spectrum of the recrystallised compound compared well with that of zirconium oxychloride octahydrate reported in the literature[6].

The BZO was prepared as follows: equimolar (0.5 M each) aqueous solutions of barium chloride and zirconium oxychloride were added to the hot solution of oxalic acid (1.0 M) which was 10% in excess. The precipitate was digested on a waterbath for 30 min, cooled and filtered, then washed with distilled water and acetone and air dried. Wet chemical analysis showed that the ratio of barium to zirconium was 1 : 1.

The acetone-washed product contained 16.16% water which corresponds to 4.5 H_2O $mole^{-1}$. The analysis of such a sample of BZO prepared under these conditions gave: Ba, 27.4; ZrO, 21.32; C_2O_4, 35.12 and H_2O, 16.16%; calculated values for BaZrO $(C_2O_4)_2 \cdot 4.5\ H_2O$: Ba, 27.38; ZrO, 21.38; C_2O_4 35.10 and H_2O, 16.15% which show that there is no noticeable deviation between calculated and observed values. Oxalate in the residue at different stages of thermal decomposition was determined by permanganate titration. Thermogravimetry (TG) was carried out using a

TABLE 1

X-RAY PATTERN OF BZO

2θ-values	*d-values (Å)*	*Intensity of peak*
21.7	4.76	St
22.8	4.53	Sm
25.00	4.13	St
26.65	3.88	M
28.8	3.60	St
30.1	3.45	M
31.65	3.28	St
34.05	3.06	Sm
34.6	3.01	Sm
35.6	2.92	Sm
36.9	2.83	M
38.2	2.73	St
39.1	2.67	Sm
39.6	2.64	Sm
41.9	2.504	St
43.05	2.44	Sm
43.6	2.41	Sm
45.1	2.33	St
46.1	2.28	St
48.2	2.19	M
50.2	2.11	M
52.1	2.03	M

St, strong; Sm, small; M, medium.

Stanton Red Croft Thermobalance and differential thermal analysis (DTA) by using a Fisher Differential Thermalyzer, Model 260P fitted with an automatic voltage stabilizer, recorder and amplifier. About 50 mg samples were taken in platinum crucibles for TG and the heating rate was 6°C min^{-1}. 150–200 mg samples were taken for DTA in a quartz crucible using calcined α-alumina as a reference material and the heating rate was 10°C min^{-1}.

Isothermal heating was carried out in a furnace fitted with a pyrometer and temperature controller. The accuracy of the temperature was ±5°C. IR spectra were recorded with a Beckman IR-20 double beam instrument in the range 250–4000 cm^{-1}, with samples in KBr pellets. The X-ray diffraction pattern was taken on a Seimens X-ray diffractometer using Co-$K\alpha$ radiation of 25 kV. It reveals that BZO is a crystalline compound. Some of the 2θ and *d*-values are given in Table 1.

RESULTS AND DISCUSSION

Figure 1 gives the DTA, TG and DTG curves for barium zirconyl oxalate hydrate (BZO). The thermogram shows that 2 moles of water of hydration are given

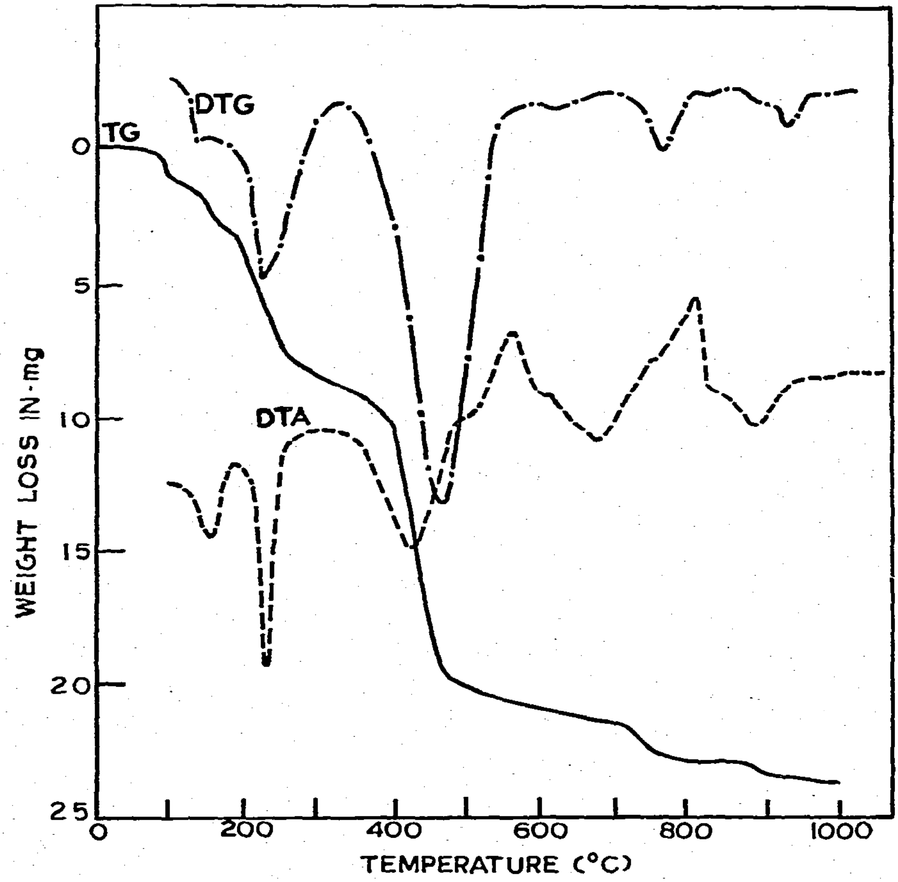

Fig. 1. DTA, TG and DTG of BZO in air.

TABLE 2

ANALYSIS OF THERMOGRAVIMETRIC CURVE

Decomposition step	*Calculated % wt. loss*	*Temperature range (°C)*	*% wt. loss in TGA*
Partial dehydration of BZO	7.18	100–190	6.80
Dehydration of BZO	8.97	190–260	8.90
Oxalate decomposition	21.65	260–460	22.50
Evolution of CO and partial decomposition of carbonate	4.97	460–760	4.90
Final decomposition of carbonate	2.2	760–920	1.98

off up to 190°C per mole of BZO and the remaining 2.5 moles are given off up to 260°C. The anhydrous barium zirconyl oxalate decomposes from 260 to 460°C to a carbonate which further decomposes in two stages (460–760°C; 760–920°C) to barium zirconate. It can be seen that 1 : 1 correlation exists between DTA and DTG curves, indicating that all the thermal effects are accompanied by weight loss. There are three major steps involved in the decomposition, these being: (1) a two-stage dehydration; (2) decomposition of the anhydrous oxalate to a carbonate; (3) the decomposition of the carbonate to barium zirconate. The DTA curve clearly shows the two stages of the dehydration process which are not indicated separately in DTG. The data for observed weight losses and the corresponding temperature ranges are given in Table 2. The different stages obtained by the thermal decomposition of BZO will now be discussed.

Dehydration

The amount of water present in excess of 4.5 mole^{-1} can be removed by washing the BZO with acetone. Such a sample gives off 2 moles of water between 100–190°C. The other 2.5 moles are driven off between 190–260°C and the anhydrous BZO is formed. The thermogram shows 15.70% weight loss, as indicated in Table 2, where the calculated value for 4.5 moles of water per mole of BZO is 16.15%. IR spectra and chemical analysis of the samples obtained isothermally at these temperatures show that the oxalate groups remain unaffected.

Decomposition of oxalate

Thermal decomposition of oxalate as such is a multi step process. The first endothermic reaction occurs between 260–460°C with 22.5% weight loss. This clearly appears on the DTA curve as an endothermic peak followed by an exothermic peak. The latter peak may be attributed to the oxidation of carbon monoxide (evolved during the decomposition process) to carbon dioxide. This stage involves a complex set of reactions which are probably decomposition of oxalate and oxidation and/or

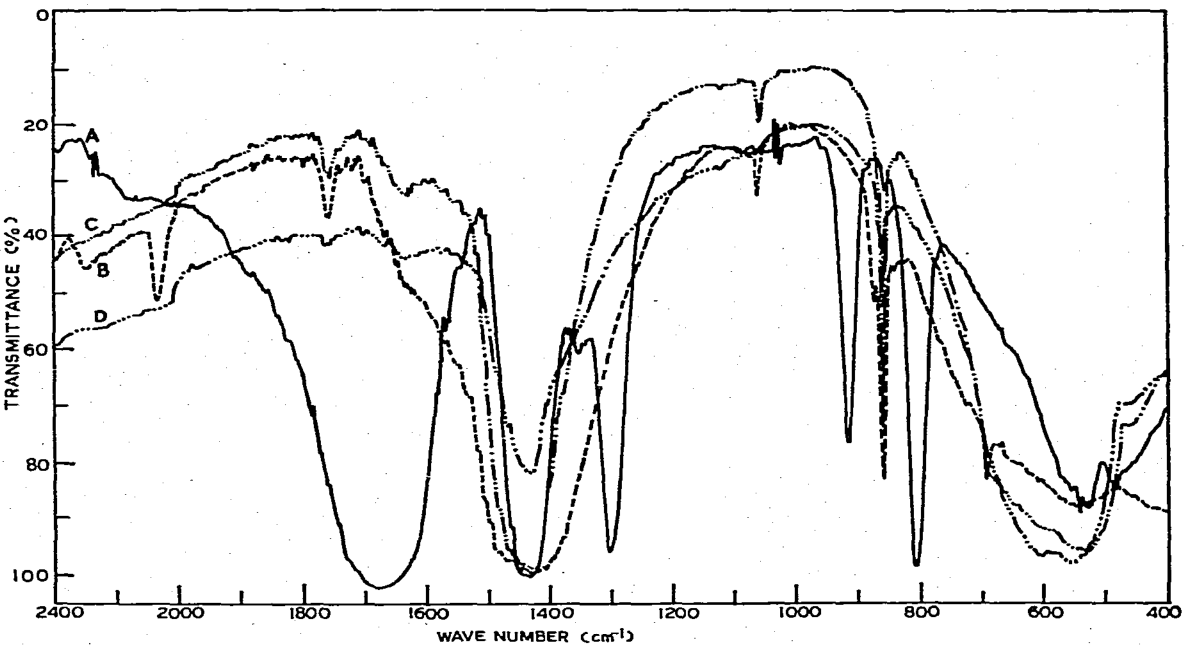

Fig. 2. IR spectra of BZO (——), BZO heated at 460°C (– – – –), residue obtained at 750°C (—..—) and 920°C (—...—).

disproportionation of carbon monoxide and the oxidation of carbon produced during the disproportionation. The residue at this stage has the composition $Ba_2Zr_2O_5CO_3 \cdot (CO)$. The sample obtained from isothermal heating at 460°C was light brown in colour, indicating that some carbon was present.

Decomposition of carbonate

Further weight loss between 460–760°C corresponds to the partial decomposition of carbonate and evolution of (trapped) carbon monoxide, which is also indicated in the DTA curve. Final decomposition of the carbonate takes place between 760–920°C.

Figure 2 gives the IR spectra of various materials. The spectrum (A) shows the principal band ν_{as} (C—O) of barium zirconyl oxalate at 1690 cm^{-1}, other bands may be assigned to different normal modes of vibrations of the oxalate group[7] and all are combination bands. The IR spectra of samples obtained at 190 and 250°C show all the bands assigned to oxalate. The chemical analysis of these samples suggests that both the oxalate groups are intact. The spectrum (B) reveals some new features: the bands at 2070 and 2300 cm^{-1} may be due to the presence of carbon monoxide and carbon dioxide gases, respectively, as both these gases are being produced in the decomposition of BZO. The lower values of the fundamental frequencies for CO and CO_2 may be due to some interaction of these gases with the lattice. The bands at 2070 and 2300 cm^{-1} are found to be missing if the IR spectra of the same sample is taken after keeping it in an oven at 75°C for several days, indicating that the CO and CO_2 present in the residue have escaped. Furthermore, the release of CO and

CO_2 at such a low temperature may indicate that these are probably present at the surface. The remaining bands are those of ionic carbonate; ν_{as} at 1450 cm^{-1}, is almost symmetrical, ν_s at 1060 cm^{-1} is weakly active. The deformation mode and deformation out-of-plane bending modes occur at 700 and 860 cm^{-1} (w.d.), respectively. The band at 1760 cm^{-1} may be a combination band [ν_s (C—O) + δ(O—C—O)].

Spectrum (C) also indicates the presence of carbonate and all the bands are assigned accordingly[8, 9]. In addition to carbonate bands a strong band occurs between 500 and 600 cm^{-1} which is assigned to zirconate. This indicates that some of the $BaZrO_3$ is formed at this stage.

Spectrum (D) of a sample heated at 920°C indicates the formation of barium zirconate[10] containing a small amount of carbonate impurity. If the sample is heated at 920°C for several hours no carbonate impurity is indicated. All the above observations and results allow us to propose a four-stage scheme for the thermal decomposition of barium zirconyl oxalate hydrate (BZO). It is as follows

$$BaZrO(C_2O_4)_2 \cdot 4.5\,H_2O \xrightarrow[100\text{–}190^\circ C]{} BaZrO(C_2O_4)_2 \cdot 2.5\,H_2O + 2H_2O \qquad (1a)$$

$$BaZrO(C_2O_4)_2 \cdot 2.5\,H_2O \xrightarrow[190\text{–}260^\circ C]{} BaZrO(C_2O_4)_2 + 2.5\,H_2O \qquad (1b)$$

$$2\,BaZrO(C_2O_4)_2 \xrightarrow[260\text{–}460^\circ C]{} Ba_2Zr_2O_5CO_3(CO) + 3CO_2 + 3CO \qquad (2)$$

$$Ba_2Zr_2O_5CO_3(CO) \xrightarrow[460\text{–}760^\circ C]{} 1/2\,Ba_2Zr_2O_5(CO_3) + BaZrO_3 + CO + 1/2\,CO_2 \qquad (3)$$

$$1/2\,Ba_2Zr_2O_5(CO_3) \xrightarrow[760\text{–}920^\circ C]{} BaZrO_3 + 1/2\,CO_2 \qquad (4)$$

Equation (1) represents the dehydration in two stages. Equation (2) corresponds to the loss of 3 moles of CO_2 and 3 moles of CO per 2 moles of BZO and formation of a carbonate. The residue at this stage of decomposition has a composition of $Ba_2Zr_2O_5CO_3(CO)$. The IR spectra (B) of this intermediate shows a band at 2070 cm^{-1} due to carbon monoxide in addition to carbonate bands. In general, the composition of this intermediate is nonstoichiometric with respect to the retained carbon monoxide, indicating that somehow the carbon monoxide may be held in the solid[11].

In step 3 carbon monoxide is released with the partial decomposition of carbonate to zirconate. The final decomposition of carbonate occurs between 760 and 920°C giving barium zirconate (step 4). From the above discussion it is clear that the weight loss steps in TG and the explanations based on them are very limited in scope and the intermediates often may not represent stable composition. The composition of residues isolated in isothermal experiments need not and often do not tally with the apparent composition assigned by weight loss measurements during thermogravimetric analysis.

ACKNOWLEDGEMENTS

The authors are grateful to Dr. I. P. Saraswat, Head of the Chemistry Department, for the research facilities.

REFERENCES

1 E. K. Keler and A. K. Kuzestov, *Zh. Prikl. Khim.*, 34 (1961) 2146; Chem. Abstr., 56 (1962) 9685.
2 Osamu Saburi, *Ceram. Abstr.*, (1962) 202j.
3 P. K. Gallagher and F. Schray, *J. Am. Ceram. Soc.*, 46 (1963) 567.
4 P. K. Gallagher and J. Thomson, Jr., *J. Am. Ceram. Soc.*, 48 (1965) 644.
5 B. V. Strizhøkov, A. V. Lapitskiĭ, L. G. Vlasov and A. I. Isvetkov, *Dokl. Akad. Nauk S.S.S.R.*, 133 (1960) 1347.
6 R. A. Nyquist and R. O. Kagel, *Infrared Spectra of Inorganic Compounds*, Academic Press, New York, London, 1971, 244 pp.
7 K. Nakamoto, *IR Spectra of Inorganic and Coordination Compounds*, Wiley, New York, 1963, pp. 210–214.
8 C. N. R. Rao, *Chemical Applications of IR Spectroscopy, Academic Press*, New York, London, 1963, 342 pp.
9 S. Bhagavantam and T. Venkatarayudu, *Proc. Ind. Acad. Sci., Sect. A*, 9 (1939) 224.
10 R. A. Nyquist and R. O. Kagel, *Infrared Spectra of Inorganic Compounds*, Academic Press, New York, London, 1971, 106 pp.
11 H. G. Gopala Krishnamurthy, M. Subba Rao and T. R. Narayanan Kutty, *J. Inorg. Nucl. Chem.*, 37 (1975) 891.