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THERMAL DECOMPOSITION OF ZIRCONYL OXALATES

I. BARIUM ZIRCONYL OXALATE

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Conditions for the preparation of stoichiometric barium zirconyl oxalate heptahydrate (BZO) have been standardized. The thermal decomposition of BZO has been investigated employing TG, DTG and DTA techniques and chemical and gas analysis. The decomposition proceeds through four steps and is not affected much by the surrounding gas atmosphere. Both dehydration and oxalate decomposition take place in two steps. The formation of a transient intermediate containing both oxalate and carbonate groups is inferred. The decomposition of oxalate groups results in a carbonate of composition $Ba_2Zr_2O_5CO_3$, which decomposes between 600 and 800° and yields barium zirconate. Chemical analysis, IR spectra and X-ray powder diffraction data support the identity of the intermediate as a separate entity.

The zirconates of bivalent metals, especially those of alkaline earths and lead, are technologically important because of their electrical properties. Generally, these zirconates are prepared by high-temperature methods and the products are usually non-stoichiometric. This has necessitated the development of low-temperature chemical methods to prepare them as high-purity materials. The analogous titanates of bivalent metals can be obtained by the thermal decomposition of the corresponding titanyl oxalates [1–5]. It is therefore interesting to look at the zirconyl oxalates as possible precursors of the metazirconates. Zirconyl oxalates could not be prepared by the coprecipitation method employed for titanyl oxalates. The method developed by Sheinkman et al. [6] always yielded a zirconium-poor precipitate Unlike titanyl oxalates, where the available literature is copious, though often contradictory, the literature on zirconyl oxalates of bivalent metals is rather scanty. This prompted the present investigation on zirconyl oxalates.

Experimental

Reagents

All reagents were either BDH Analar or E Merck "Pro analyse" grade chemicals. Barium zirconyl oxalate heptahydrate (BZO) was prepared as follows: The acid $H_2ZrO(C_2O_4)_2 \cdot 3\,H_2O$ was prepared by the method of Zaitsev et al. [7, 8]. The acid was ammoniated by passing dry ammonia, diluted with nitrogen, over the solid [9a] to get $(NH_4)_2ZrO(C_2O_4)_2 \cdot 3\,H_2O$. Freshly-prepared ammonium salt was dissolved in water (2.444 mg Zr ml^{-1}) and the pH was adjusted to 6. This

Table 1

Effects of concentrations of reagents and pH on the stoichiometry of the precipitated barium zirconyl oxalate

The nature of barium in solution	Ba	NZO	pH	Ba	Zr	C_2O_4
	before precipitation			in the precipitate		
As chloride	1.5	1	2.5	0.81	1	2.12
	1.0	1	3.0	0.81	1	1.96
	1.5	1	4.6	0.89	1	2.06
As acetate	1.5	1	5.5	0.91	1	1.98
	2.0	1	5.0	0.90	1	1.98
	2.0	1	5.5	0.95	1	1.99
	2.0	1	6.0	1.00	1	1.99

solution was added to a solution of barium acetate (7.364 mg Ba ml^{-1}) at pH 6. The stoichiometry of the precipitate depends on the pH and the ratio of Ba : Zr in the solution (Table 1). The precipitate was washed several times with distilled water and filtered. It was finally washed with acetone and air-dried. The air-dried sample corresponds to the composition $BaZrO(C_2O_4)_2 \cdot 7\,H_2O$. The analysis of such a sample gave the following results: Ba: 24.91; ZrO: 21.2; C_2O_4: 32.02; and H_2O: 23.2 per cent. Calculated values for $BaZrO(C_2O_4)_2 \cdot 7\,H_2O$ are Ba: 25.14; ZrO: 21.34; C_2O_4: 32.2; and H_2O: 23.04 per cent. X-ray powder diffraction data on BZO are presented in Table 2.

Table 2

X-ray powder diffraction data on barium zirconyl oxalate heptahydrate

Sl No.	d, Å	I/I_0^*
1	6.21	s
2	4.71	m
3	4.12	s
4	3.840	w
5	3.559	m
6	3.393	w
7	3.307	w
8	3.146	w
9	3.025	w
10	2.825	m
11	2.723	m
12	2.509	m
13	2.330	m
14	2.270	m

* The intensities are visual estimates only

Analysis

The oxalate was decomposed by gentle heating and the residue brought into solution with hydrochloric acid. Barium was precipitated as the sulphate and weighed as $BaSO_4$, while zirconium was precipitated with cupferron, ignited and weighed as ZrO_2. Oxalate was estimated by titration with permanganate. Carbonate was determined by decomposing it with hydrochloric acid and absorbing the evolved carbon dioxide, after drying, in ascarite. The gaseous products of decomposition were analysed by employing a conventional vacuum manifold with calibrated dead-space. The total volume of the gases evolved at any given temperature could be determined. As carbon monoxide and carbon dioxide were the only gases evolved, their ratio was measured as follows. After recording of the total pressure of the gases, carbon dioxide was condensed by means of a liquid nitrogen trap, and uncondensed carbon monoxide was pumped out. The cold trap was removed and the pressure developed was recorded. From the difference, the proportion of carbon monoxide was estimated.

Instrumental methods

Thermogravimetric analysis in flowing atmospheres of air, nitrogen and carbon dioxide, and in a vacuum, was carried out on a manual thermobalance which employed a sensitive quartz spring. The experimental set-up was similar to that of Hooley [9]. Sample weights were ca. 150 mg. DTA in different atmospheres and in a vacuum was carried out in a unit similar to that of Lodding and Hammel [10]. Sample weights were ca. 400 mg.

IR spectra in the range 400–4000 cm^{-1} were recorded with a Carl-Zeiss Jena UR 10 double-beam instrument, with samples in both Nujol mull and alkali halide pellets. X-ray diffraction patterns were recorded photographically, using a Philips Debye-Scherrer camera of 57.3 mm diameter and nickel-filtered copper K_α radiation from a Rich-Seifert Iso Debyeflex X-ray unit.

Results

The DTA curves of BZO in different atmospheres are shown in Fig. 1. Figure 2 shows the DTG curves. The one-to-one correspondence between the DTA and DTG curves indicates that all the thermal effects are accompanied by weight losses. There are three principal steps in the decomposition, the likely reactions being (i) dehydration, (ii) decomposition of the oxalate to an intermediate carbonate, and (iii) decomposition of the carbonate to barium zirconate. These three major events remain unaffected by the nature of the surrounding atmosphere, except that the oxalate decomposition is exothermic in air. The complete data for the observed weight losses and the corresponding temperature ranges are given in Table 3.

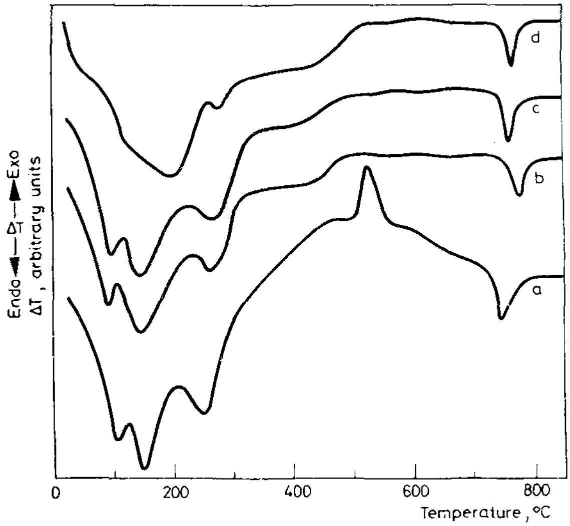

Fig. 1. DTA on BZO in (a) air, (b) carbon dioxide, (c) nitrogen and (d) a vacuum

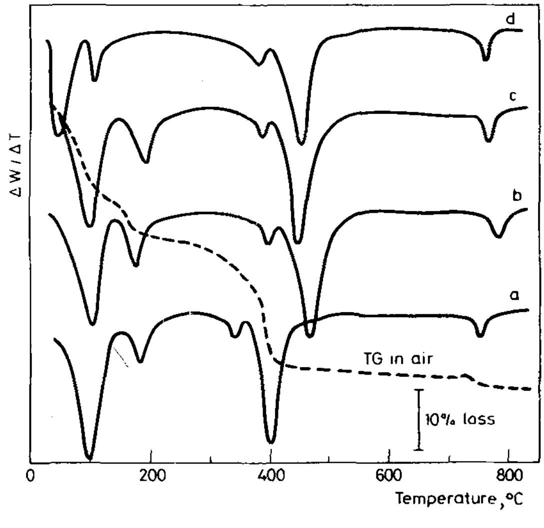

Fig. 2. DTG on BZO in (a) air, (b) carbon dioxide, (c) nitrogen and (d) a vacuum

Dehydration of the hydrate

Dehydration takes place in two steps. In the temperature range 25—120°, five moles of water of hydration are lost. Anhydrous BZO is formed in the temperature range 120—200°. In vacuum both the dehydration steps are complete around

Table 3

Gas atmosphere		Air		Carbon dioxide		Nitrogen		Vacuum	
Decomposition step	Calculated % wt. loss	Temp. range in °C	% wt. loss	Temp. range, °C	% wt. loss	Temp. range, °C	% wt. loss	Temp. range in °C	% wt. loss
Dehydration	23.03	25–195	23.5	25–180	23.0	25 – 200	23.0	25 - 125	22.5
Initial oxalate decomposition	3.83	200 – 360	2.5	180 – 390	3.0	200 – 380	3.0	200 - 375	3.75
Main oxalate decomposition	18.48	360–500	19.0	390–525	19.5	380 – 525	19.5	375 - 500	19.5
Final decomposition of the carbonate	4.03	600 - 800	4.5	600 – 800	3.5	600 - 800	4.0	600 - 800	4.3
Total weight loss	49.37		49.5		49.0		49.5		49.8

125°. The observed weight losses are in the range 22.5 to 23.5 per cent, in reasonable agreement with the calculated value of 23.03 per cent for the removal of 7 H_2O mole^{-1}. The first step of dehydration is reversible, whereas the second step is irreversible. BZO is crystalline, but the anhydrous material is poorly crystalline. However, the material is non-porous, as revealed by its low surface area of 2.0 m^2g^{-1}.

Decomposition of the oxalate

Thermal decomposition of the oxalate is a two-step process. The first endothermic reaction occurs from 200 to 380°, with a weight loss of 3 per cent. Analysis of the gas evolved when anhydrous BZO is decomposed at 320° shows that only carbon monoxide, amounting to 0.75 mole per mole BZO, is evolved. This step is endothermic even in air. Two explanations are possible for the endothermic nature. The decomposition takes place virtually in an atmosphere of water vapour from the preceding dehydration step. Alternatively, the oxidation of carbon monoxide takes place at a higher temperature. The DTA of completely dehydrated BZO in air and in a vacuum (Fig. 3) shows the first oxalate decomposition step to be endothermic in both. Dehydrated BZO is packed into the stainless steel sample holder, the furnace is maintained at 125° and the DTA assembly is evacuated to drive out all adsorbed moisture from the sample. Air is admitted to the system and DTA carried out. The results are similar to those of Fig. 3(a). This establishes that the gas phase oxidation of carbon monoxide does not occur in this temperature range. The residue at this stage has an apparent composition $Ba_2Zr_2O_2(C_2O_4)_{2.5}(CO_3)_{1.5}$ and could not be isolated as a stable intermediate. The second stage of oxalate decomposition, which is expected to be the major event in the thermoanalytical experiments [1], is not prominent in the DTA curves, though it is prominent in DTG. This occurs in the temperature range of 360 to 525°, with a weight loss of 19.0 to 19.5 per cent in different gas atmospheres. The

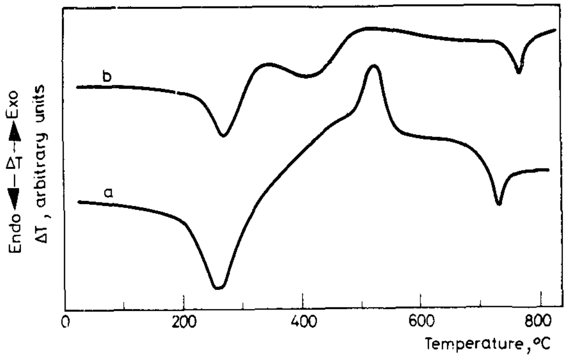

Fig. 3. DTA on anhydrous BZO in (a) air and (b) a vacuum

shallow DTA peaks might be due to the wide temperature range of decomposition, or it might be inherently a low-enthalpy process. Analysis of the gaseous products shows that both carbon monoxide and carbon dioxide are simultaneously evolved. A complex set of reactions takes place at this stage of oxalate decomposition, which involves oxidation and/or disproportionation of carbon monoxide, and oxidation of carbon (in air) produced during the disproportionation of carbon monoxide, in addition to the decomposition of the oxalate. Because of these multiple processes, the total weight loss is variable, depending on the surrounding gas atmosphere. The oxalate decomposition is endothermic in all other atmospheres but air. In air the endotherm is masked by the highly exothermic oxidation of carbon monoxide. The residue at this stage has a composition $Ba_2Zr_2O_5CO_3$. The residue is white when BZO is decomposed in air, but is brown to black if the decomposition is carried out in a vacuum or an inert atmosphere. The colour of the residue is due to the presence of traces of elemental carbon. Isothermal heating of BZO at 450° for 48 hours yielded a residue of the same composition. The chemical analysis of the residue gave the following results: Ba: 45.82, ZrO_2: 20.72 and CO_2: 7.43 per cent; calculated values for $Ba_2Zr_2O_5CO_3$ are Ba: 46.01, ZrO_2: 20.63 and CO_2: 7.37 per cent. The residue is crystalline and the reflections in the X-ray powder diffraction pattern (Table 4) do not correspond to the strongest reflections of barium carbonate, zirconium dioxide or barium zirconate. Thus, the residue is not a mixture of barium carbonate and zirconium dioxide, but a separate compound.

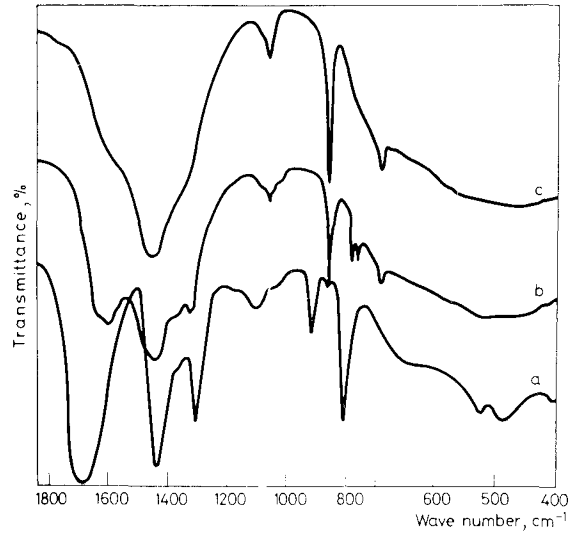

Fig. 4. IR spectra of (a) BZO, (b) $Ba_2Zr_2O_2(C_2O_4)_{2.5}(CO_3)_{1.5}$ and (c) $Ba_2Zr_2O_5CO_3$

Figure 4 gives the IR spectra of BZO and of the different intermediates. The principal band of BZO (Fig. 4a) is the symmetric stretching frequency of the C–O group of the oxalate at 1680 cm^{-1}. Other bands, which are all combination bands, are attributable to different normal modes of vibration of the oxalate group. Spectrum C is that of a true ionic carbonate; the ν_{as} at 1445 cm^{-1} is nearly symmetrical, ν_s at 1065 cm^{-1} is weakly active, and the deformation mode and the out-of-plane bending mode occur at 695 cm^{-1} and 865 cm^{-1}, respectively. None of the intermediates show absorption in the region 1800–2200 cm^{-1} (characteristic of free carbon monoxide or coordinated carbonyl groups). In addition there is no absorption band in the region 2200–2400 cm^{-1}, indicating the absence of entrapped carbon dioxide. Spectrum b, which is for the residue from the first stage of oxalate decomposition, exhibits the absorptions of both oxalate and carbonate groups.

Decomposition of the intermediate carbonate

The carbonate $Ba_2Zr_2O_5CO_3$ decomposes between 600 and 800° with the evolution of carbon dioxide, giving rise to barium zirconate irrespective of the nature of the surrounding gas atmosphere. The final endotherm in DTA corresponds to this step. The decomposition is shifted to a higher temperature in carbon dioxide atmosphere. The temperature of decomposition is also slightly higher in a vacuum, contrary to expectations. The observed weight loss for the carbonate decomposition varies from 3.5 to 4.5 per cent, as against the calculated loss of 4.03 per cent. The end-product is crystalline barium metazirconate.

Discussion

The thermal decomposition of barium zirconyl oxalate of doubtful stoichiometry has been investigated by Sheinkman et al. [6], who have proposed the following scheme for its decomposition:

$$BaZrO(C_2O_4)_2 \cdot 5\,H_2O \xrightarrow{140^\circ} BaZrO(C_2O_4)_2 \cdot 3\,H_2O + 2\,H_2O \qquad (1)$$

$$BaZrO(C_2O_4)_2 \cdot 3\,H_2O \xrightarrow{240^\circ} BaZrO(C_2O_4)_2 + 3\,H_2O \qquad (2)$$

$$BaZrO(C_2O_4)_2 \xrightarrow{380^\circ} BaCO_3 + ZrO_2 + 2\,CO + CO_2 \qquad (3)$$

$$BaCO_3 + ZrO_2 \xrightarrow{400-600^\circ} BaZrO_3(CO) + 1/2\,O_2 \qquad (4)$$

$$BaZrO_3(CO) \xrightarrow{600-900^\circ} BaZrO_3 + CO \qquad (5)$$

Those investigators employed a sample of barium zirconyl oxalate precipitated in a strongly acid medium. As has been pointed out earlier, the precipitate in strongly acidic media will be deficient in zirconium. Such a sample has been observed to give rise to barium carbonate as one of the decomposition products. In fact, the evidence adduced for step(4)of the reaction is the presence of a weak line attributable to $BaCO_3$ in the X-ray powder diffraction pattern of the residue. In the present study there is no evidence for any intermediate containing CO. Gas analysis at no stage shows oxygen as one of the constituents. During the final stages of the decomposition, only carbon dioxide is detected, and all evidence points to a true thermal decomposition of a carbonate rather than a reaction between two solid intermediates.

Recently, Reddy and Mehrotra [16] investigated the thermal decomposition of barium zirconyl oxalate hydrate and proposed the following scheme for its decomposition:

$$BaZrO(C_2O_4)_2 \cdot 4.5\,H_2O \xrightarrow{100-190^\circ} BaZrO(C_2O_4)_2 \cdot 2.5\,H_2O + 2\,H_2O \tag{1}$$

$$BaZrO(C_2O_4)_2 \cdot 2.5\,H_2O \xrightarrow{190-260^\circ} BaZrO(C_2O_4)_2 + 2.5\,H_2O \tag{2}$$

$$2\,BaZrO(C_2O_4)_2 \xrightarrow{260-460^\circ} Ba_2Zr_2O_5CO_3(CO) + 3\,CO_2 + 3\,CO \tag{3}$$

$$Ba_2Zr_2O_5CO_3(CO) \xrightarrow{460-760^\circ} 1/2\,Ba_2Zr_2O_5CO_3 + BaZrO_3 + + CO + 1/2\,CO_2 \tag{4}$$

$$1/2\,Ba_2Zr_2O_5CO_3 \xrightarrow{760-920^\circ} BaZrO_3 + 1/2\,CO_2 \tag{5}$$

Our results substantiate qualitatively the two-stage dehydration and the final decomposition step leading to the formation of barium metazirconate. There is no evidence in our investigation to substantiate the formation of any intermediate containing either CO or CO_2. The evidence of Reddy and Mehrotra [16] also shows that CO and CO_2 are merely adsorbed on the surface. This leads one to infer that the residues employed by them for infrared spectra had not been heated to constant weight/composition. Hence, the compound $Ba_2Zr_2O_5CO_3(CO)$ cannot be compared to the stable entity $Ba_2Ti_2O_5CO_3(CO_2)_x$ [1]. Step (4) would mean that, by isothermal heating, one should be able to isolate a mixture of $Ba_2Zr_2O_5CO_3$ and $BaZrO_3$ in the mole ration 0.5 : 1. We have not been able to isolate such a stoichiometric mixture. The decomposition of the carbonate is found to occur in one step only.

The results of the present investigation indicate the following scheme for decomposition in air:

$$BaZrO(C_2O_4)_2 \cdot 7\,H_2O \overset{25-120^\circ}{\rightleftharpoons} BaZrO(C_2O_4)_2 \cdot 2\,H_2O + 5\,H_2O \quad (1)$$

$$BaZrO(C_2O_4)_2 \cdot 2\,H_2O \xrightarrow{120-200^\circ} BaZrO(C_2O_4)_2 + 2\,H_2O \quad (2)$$

$$2\,BaZrO(C_2O_4)_2 \xrightarrow{200-360^\circ} Ba_2Zr_2O_2(C_2O_4)_{2.5}(CO_3)_{1.5} + 1.5\,CO \quad (3)$$

$$Ba_2Zr_2O_2(C_2O_4)_{2.5}(CO_3)_{1.5} \xrightarrow{360-500^\circ} Ba_2Zr_2O_5CO_3 + 2.5\,CO + 3\,CO_2 \quad (4)$$

$$Ba_2Zr_2O_5CO_3 \xrightarrow{500-800^\circ} 2\,BaZrO_3 + CO_2 \quad (5)$$

Equations (1) and (2) represent the dehydration steps. Equation (3), representing the first stage of decomposition of the oxalate, corresponds to the loss of only carbon monoxide and the formation of an oxalato-carbonate intermediate. The formation of this intermediate suggests the non-equivalence of the two oxalate groups in the structure of BZO. The non-equivalence also accounts for the two-step decomposition of the oxalate. Equation (4) represents the second step in the oxalate decomposition. Complete decomposition of the oxalate at this stage evolves both carbon monoxide and carbon dioxide in the limiting mole ratio 2.5 : 3. The actual ratio of these gases, as well as the accompanying thermal effects, are influenced by the secondary reactions of carbon monoxide. The observed ratio of CO/CO_2 is 0.65, as against the expected ratio of 0.83. This is accounted for by the disproportionation of carbon monoxide, which is known to be catalysed by transition metal oxides. It has been reported by Glasner and Steinberg [11] that as much as 70 per cent of the evolved carbon monoxide disproportionates in the decomposition of lanthanide oxalates. Complete destruction of the oxalate produces the carbonate $Ba_2Zr_2O_5CO_3$. The isolation of the intermediate $Ba_2Zr_2O_5CO_3$ by isothermal heating, and its unequivocal identification by chemical analysis and its distinct X-ray powder diffraction pattern, has provided indisputable evidence against the previous postulate [6] that the formation of $BaZrO_3$ is through a solid-state reaction between barium carbonate and zirconium dioxide.

The final step is the decomposition of the intermediate carbonate yielding barium zirconate and carbon dioxide. This decomposition is shifted to higher temperatures in carbon dioxide atmosphere. This is to be expected for the decomposition of a true carbonate and further eliminates the possibility of a solid-state reaction between barium carbonate and zirconia. The end-product is crystalline barium zirconate.

The various schemes [12–15] proposed for the thermal decomposition of barium titanyl oxalate tetrahydrate (BTO), a close analogue of BZO, invariably en-

Table 4

X-ray powder diffraction data on $Ba_2Zr_2O_5CO_3$

Sl No.	d, Å	I/I_0^*
1	3.593	s
2	3.206	w
3	2.608	s
4	2.146	m
5	2.094	w
6	2.043	w
7	2.010	m
8	1.937	m
9	1.372	m

* The intensities are visual estimates only

visage a solid-state reaction between barium carbonate and titanium dioxide as the step producing barium titanate. The evidence mostly was a faint line attributable to barium carbonate in the ill-defined X-ray powder diffraction patterns. As has been shown for non-stoichiometric BZO, titania-poor samples of BTO do produce traces of barium carbonate on heating. We have shown in an earlier paper [1] that, during the decomposition of stoichiometric BTO, an intermediate of composition $Ba_2Ti_2O_5CO_3$ is formed. This intermediate was non-crystalline and its identity had to be established by chemical analysis, the mode of further decomposition and the absence of lines due to $BaCO_3$ and TiO_2 in the X-ray patterns. The identification of $Ba_2Zr_2O_5CO_3$ as a distinct species leads us to conclude logically that the analogous $Ba_2Ti_2O_5CO_3$ is a distinct compound, and not a mixture of barium carbonate and titanium dioxide.

Though the general pattern of decomposition of BZO is similar to that of BTO, there are some significant differences. Dehydration of BZO takes place in two steps, the first stage of oxalate decomposition leading to an oxalato-carbonate is quite prominent, and the intermediates obtained during the decomposition of BZO are all crystalline except for the oxalato-carbonate. The residues do not show any tendency to retain carbon dioxide in the solid matrix, unlike the non-crystalline residues obtained in the decomposition of barium titanyl oxalate [1].

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RÉSUMÉ — On a standardisé les conditions de préparation de l'oxalate heptahydraté de zirconyle et de baryum (BZO) stoechiométrique. On a étudié la décomposition thermique de BZO par TG, TGD et ATD ainsi que par analyses chimiques et analyses des gaz. La décomposition a lieu en quatre étapes et n'est pas trop influencée par l'atmosphère ambiante. La déshydratation et la décomposition de l'oxalate ont lieu en deux étapes. Il se forme un composé intermédiaire de transition contenant à la fois les groupes oxalate et carbonate. La décomposition des groupes oxalate fournit un carbonate de composition $Ba_2Zr_2O_5CO_3$ qui se décompose entre 600 et 800° pour fournir du zirconate de baryum. L'analyse chimique, les spectres IR et la diffraction des rayons X sur poudre, apportent les preuves de l'existence d'un composé intermédiaire comme entité séparée.

ZUSAMMENFASSUNG — Die Bedingungen für die Herstellung von stöchiometrischem Bariumzirconyl-oxalat Heptahydrat (BZO) wurden standardisiert. Die thermische Zersetzung von BZO wurde unter Einsatz der TG-, DTG- und DTA, sowie der chemischen und Gasanalyse untersucht. Die Zersetzung verläuft über vier Stufen und wird von der umgebenden Gasathmosphäre nicht besonders beeinflusst. Sowohl die Dehydratisierung als auch die Oxalatzersetzung erfolgt in zwei Stufen. Die Bildung einer intermediären Übergangsverbindung mit sowohl Oxalat- als auch Carbonatgruppen wirken hierbei mit. Die Zersetzung der Oxalatgruppen ergibt ein Carbonat der Zusammensetzung $Ba_2Zr_2O_5CO_3$, das zwischen 600 und 800° zersetzt wird und Bariumzirconat ergibt. Die Angaben der chemischen Analyse, der IR-Spekren und der Röntgen-Pulver-Diffraktion unterstützen die Identität der Intermediärverbindung als eine separate Einheit.

Резюме — Стандартизированы условия получения гептагидрата цирконил оксалата бария (БЦО) стехиометрического состава. Термическое разложение БЦО было изучено методами ТГ, ДТГ и ДТА, а также химическим и газовым анализом. Разложение протекает в четыре стадии и не затрагивается намного окружающей газовой атмосферой. Дегидратация и разложение оксалата протекает в две стадии. Сделано заключение об образовании неустойчивого промежуточного продукта, содержащего одновременно обе оксалатную и карбонатную группы. Разложение оксалатных групп приводит к карбонату состава $Ba_2Zr_2O_5CO_3$, который разлагается между 600—800 с образованием цирконата бария. Данные химического анализа, ИК спектров и порошковой рентгенографии доказывает подлинность промежуточного продукта как самостоятельной единицы.