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THE THERMAL DECOMPOSITION OF OXALATES. PART 18 *. THE PREPARATION AND THERMAL DECOMPOSITION OF ACID BARIUM OXALATES

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ABSTRACT

This study entails the preparation of various forms of barium oxalate. The main method of preparation used was the simultaneous mixing of equimolar solutions of barium chloride and oxalic acid over a range of concentrations of starting materials from 0.2 to 1.6 mol. Each compound was analysed for its percentage of barium, oxalate and water content. Thermogravimetric and differential thermal analysis data were obtained and the results verified by comparison with chemical analysis data. It is shown that varying the conditions of preparation produces forms of barium oxalate differing in chemical composition.

INTRODUCTION

Barium oxalate has been reported to exist in two distinct forms: first, the neutral barium oxalate with various hydrated forms; and second, the acid salts of barium oxalate. The list of the different oxalates is given in Table 1. The form generally reported is the hemihydrate [1] which is a white crystalline solid. However, the monohydrate, dihydrate and trihydrate have also been reported. They are also white crystalline solids. The acid oxalates of barium are also listed in Table 1, these have been studied by Walter-Levy and Laniepce [2], Mutin and Watelle-Marion [3] and, again, are white crystalline materials.

The acid salts $BaC_2O_4 \cdot H_2C_2O_4 \cdot 2\ H_2O$ have been prepared by Brunhs [4] from a mixture of oxalic acid/barium chloride (2 : 1). On further addition of barium chloride and oxalic acid, needles of the acid salt separate out. With diminishing acid content the compounds $Ba(C_2O_4)_2 \cdot H_2C_2O_4 \cdot 2\ H_2O$ [4]

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* For part 17, see Thermochim. Acta, 58 (1982) 191.

and $Ba_8(C_2O_4)_3 \cdot H_2C_2O_4 \cdot 3\ H_2O$ [4] were obtained. The acid oxalates $2(BaC_2O_4 \cdot H_2C_2O_4) \cdot 2\ H_2O$ and $BaC_2O_4 \cdot H_2C_2O_4 \cdot 2\ H_2O$ were formed by the addition of barium ions to a solution containing oxalates at pH 2.5–1 [2]. The former changes to the latter at a lower pH.

The thermogravimetric analysis of acid barium oxalate has been studied by Zagorchev [5] using a starting material of formula $BaC_2O_4 \cdot H_2C_2O_4 \cdot 2\ H_2O$. He found the decomposition occurred in a stepwise manner: first, loss of water; followed by the loss of 3/4 molecule of oxalic acid which resulted in the formation of a new intermediate; and finally the formation of the carbonate.

Thermogravimetric analysis and X-ray measurements of acid barium oxalate were also carried out by Mutin and Watelle-Marion [3].

EXPERIMENTAL

Preparation of barium oxalate

Barium oxalate can be prepared by mixing solutions of barium chloride and sodium oxalate. In this series of experiments however, the barium oxalate was prepared by the reaction of barium chloride and oxalic acid solutions. A series of samples were prepared using equimolar solutions of barium chloride and oxalic acid. The series of samples were prepared from reaction solutions ranging from 0.2 to 1.6 mol l^{-1} starting material.

TABLE 1

The concentrations of the starting materials, weight of barium chloride and oxalic acid used, weight of acid barium oxalate precipitated, the label for each sample and the percentage yield based on half the molarity of barium chloride for each sample

Starting concentration (mol)	Weight of $BaCl_2 \cdot H_2O$	Weight of $H_2C_2O_4 \cdot 2\ H_2O$	Weight of precipitate	Label for each sample	% Yield based on half molarity of $BaCl_2$
0.2	48.8	25.2	32.95	BaOX1	93.87
0.4	97.6	50.4	48.60	BaOX2	69.0
0.5	122.0	63.0	67.70	BaOX3	77.0
0.6	146.4	75.6	86.20	BaOX4	82.0
0.7	168.8	88.2	96.10	BaOX5	73.0
0.8	195.2	100.8	88.05	BaOX6	64.0
1.0	244.0	126.0	130.20	BaOX7	77.0
1.1	268.2	138.6	161.50	BaOX8	84.0
1.2	292.8	151.2	173.20	BaOX9	82.0
1.3	327.2	163.8	180.70	BaOX10	82.0
1.4	341.6	176.4	190.70	BaOX11	79.0
1.6	390.4	201.6	199.50	BaOX12	72.0

Solutions of equimolar barium chloride and oxalic acid were prepared at room temperature. A pair of separating funnels were used, delivering 200 ml of each solution simultaneously. Using these funnels, barium chloride and oxalic acid solutions were run together into a 5-l beaker and stirred by means of a magnetic stirrer. With the starting material in a concentration range of 0.2–1.6 mol l^{-1} a white precipitate was obtained immediately. One litre of each reactant was used. The yield of the reaction is noted in Table 1.

Each sample of barium oxalate was labelled for further reference, e.g., acid barium oxalate prepared from 0.2 mol l^{-1} barium chloride and 0.2 mol l^{-1} oxalic acid was designated BaOXl. The designations are listed in Table 1. Table 1 also lists the percentage yield based on half the molarity of barium chloride and a formula of $BaC_2O_4 \cdot H_2C_2O_4 \cdot 2\ H_2O$ for acid barium oxalate. The percentage oxalate in each sample is listed in Table 1.

When looked at under a microscope, the crystals of acid barium oxalate were found to be needle-like in shape. The acid salt was washed using 1 g of sample to 100 cm^3 of distilled water and the salt was re-analysed. The analysis showed the loss of an oxalic acid molecule and water of crystallisation to leave barium oxalate hemihydrate.

The preparation of barium oxalate by other methods

In this section various alternative methods of preparing barium oxalate are discussed. The effect of adding an oxalic acid solution to a barium chloride solution and vice versa are investigated. The preparation of barium oxalate using other starting materials was also investigated.

Methods of preparation

(1) Solutions of 0.25 mol l^{-1} barium chloride and 0.25 mol l^{-1} sodium oxalate were mixed together as before. A series of solutions of different starting material concentrations were considered as an extension of this investigation but due to the very low solubility of the sodium oxalate only one concentration was prepared, as shown above. The resultant precipitate was filtered off and dried below 80 °C.

(2) A 1-mol l^{-1} solution of barium chloride was added to a 1-mol l^{-1} solution of oxalic acid and the precipitate was filtered off and dried below 80 °C.

(3) A 1-mol l^{-1} solution of oxalic acid was added to a 1-mol l^{-1} solution of barium chloride and the precipitate collected as described in (2) above.

(4) A 0.25-mol l^{-1} oxalic acid solution was mixed with a 0.25-mol l^{-1} barium nitrate solution as described earlier and again the precipitate collected as already described.

(5) A 0.25-mol l^{-1} oxalic acid solution was mixed with 0.25-mol l^{-1} barium hydroxide solution as earlier. The precipitate was treated as above.

TABLE 2

The percentage of oxalate, barium and water found in each compound and the method of preparation

Method of preparation [a]	Percentage of oxalate	Percentage of barium	Percentage of water
1	39.2	56.4	4.4
2	51.6	39.8	8.6
3	51.6	39.8	8.6
4	51.6	39.8	8.6
5	51.6	39.8	8.6
6	39.2	56.4	4.4

[a] (1) Barium content based on $BaC_2O_4 \cdot H_2O$ is 56.43%; (2) barium content based on $BaC_2O_4 \cdot 0.5\ H_2O$ is 58.6%; (3) barium content based on $BaC_2O_4 \cdot H_2C_2O_4 \cdot 2\ H_2O$ is 39.08%; (4) oxalate content based on $BaC_2O_4 \cdot H_2O$ is 36%; (5) oxalate content based on $BaC_2O_4 \cdot 0.5\ H_2O$ is 37.6%; (6) oxalate content based on $BaC_2O_4 \cdot H_2C_2O_4 \cdot 2\ H_2O$ is 50.7%; (7) water content based on $BaC_2O_4 \cdot H_2O$ is 7.4%; (8) water content based on $BaC_2O_4 \cdot 0.5\ H_2O$ is 3.84%; (9) water content based on $BaC_2O_4 \cdot H_2C_2O_4 \cdot 2\ H_2O$ is 10.25%.

(6) A 0.1-mol l^{-1} oxalic acid solution was mixed with a 0.1-mol l^{-1} barium chloride solution as described earlier and the precipitate collected as already described.

Analysis

The compounds were analysed for barium content, water content and oxalate content as before. The results are listed in Table 2 and the method of preparation, shown as (1), (2), etc.

Table 3 lists the method of preparation, shown as (1), (2) etc., the formula for each compound obtained and the determination of its molecular weight.

Thermal analysis equipment

The apparatus used to perform the differential thermal analysis (DTA) experiments was the Netszch unit, using dead burned alumina as the

TABLE 3

The method of preparation shown, the formula for each compound and the molecular weight

Method of preparation	Molecular formula	Molecular weight
1	$BaC_2O_4 \cdot H_2O$	243.44
2	$BaC_2O_4 \cdot H_2C_2O_4 \cdot 1.66\ H_2O$	345.3
3	$BaC_2O_4 \cdot H_2C_2O_4 \cdot 1.66\ H_2O$	345.3
4	$BaC_2O_4 \cdot H_2C_2O_4 \cdot 1.66\ H_2O$	345.3
5	$BaC_2O_4 \cdot H_2C_2O_4 \cdot 1.66\ H_2O$	345.3
6	$BaC_2O_4 \cdot H_2O$	243.44

reference. Thermogravimetric analysis (TG) experiments were performed on the Stanton-Redcroft TG-750.

RESULTS AND DISCUSSION

The results, discussed in detail later, are best understood in terms of the two following general schemes of decomposition.

(1) Barium oxalate hemihydrate

The steps involving weight loss are those that may be detected in the TG experiments. In the case of dehydration, this may be represented as

$BaC_2O_4 \cdot \frac{1}{2}\ H_2O \rightarrow BaC_2O_4 + \frac{1}{2}\ H_2O$ (weight loss = 3.84%)

This is followed by the conversion to barium carbonate

$BaC_2O_4 \rightarrow BaCO_3 + CO$ (weight loss = 11.5%)

(2) Acid Barium oxalate

Again the water is lost first

$BaC_2O_4 \cdot H_2C_2O_4 \cdot 2\ H_2O \rightarrow BaC_2O_4 \cdot H_2C_2O_4 + 2\ H_2O$ (weight loss = 10.25%)

Followed by the loss of oxalic acid

$BaC_2O_4 \cdot H_2C_2O_4 \rightarrow BaC_2O_4 + H_2C_2O_4$ (weight loss = 25.62%)

The final step is the loss of carbon monoxide to form the carbonate

$BaC_2O_4 \rightarrow BaCO_3 + CO$ (weight loss = 7.97%)

Again these are general and schematic but a detailed examination of the results in this investigation confirms the existence of these steps and the order of their appearance.

The DTA's and TG's for most of the samples were run at a heating rate of $10\,^{\circ}C\ min^{-1}$. The DTA curve for both acid barium oxalate and barium oxalate hemihydrate were carried out under a nitrogen atmosphere; the only difference in the resulting DTA curves was an endothermic reaction for the loss of carbon monoxide in nitrogen instead of an exothermic reaction in air.

The DTA curve for barium oxalate hemihydrate gave the three expected peaks and the TG the two expected weight losses. The DTA curve for acid barium oxalate gave the four expected peaks and the TG curve gave the three expected weight losses. The TG curve of the acid salt left a white deposit on the cooler part of the tube; on analysis this was found to be oxalic acid. The percentage weight loss and the substance lost is shown in Tables 4 and 5. Table 6 lists the starting and ending temperatures for each of

TABLE 4

The percentage weight loss, substance loss and the calculated molecular weight for each compound

Compound	% Weight loss of water	% Weight loss of oxalic acid	% Weight loss of CO	Molecular weight
BaOX1	11.0	10.0	10.0	280
BaOX2	9.0	24.0	8.0	350
BaOX3	9.0	25.0	8.0	350
BaOX4	10.0	26.0	9.0	311
BaOX5	9.0	25.0	8.0	350
BaOX6	9.0	26.0	8.0	350
BaOX7	10.0	25.0	7.75	361
BaOX8	9.0	25.0	8.0	350
BaOX9	9.0	26.0	7.75	361
BaOX10	9.0	25.0	8.0	350
BaOX11	9.0	25.0	8.0	350
BaOX12	9.0	26.0	7.75	361
BaOX13	4.0	–	12.0	233

the weight losses. Table 7 lists the starting and ending temperatures for each of the DTA peaks.

The DTA curves showed four peaks for the acid barium oxalate compounds. The second peak was endothermic and in all of the acid salts it was complex. The overall peak varies from two to four smaller peaks. The third peak was exothermic in air and endothermic in nitrogen, in some of the samples it consisted of one large peak and one very small peak at the end. The fourth peak was a result of the phase change occurring in the carbonate.

TABLE 5

The component lost, the type of peak and the peak temperature for all the samples listed (phase change = 812 in all cases)

Sample	Loss of water (endo)	Loss of oxalic acid (endo)	Loss of CO (exo)
BaOX1	182, 212	270 (exo)	370 (endo), 462
BaOX2	120, 160	220, 240, 254, 262	440
BaOX3	116, 170	230, 240, 262	460
BaOX4	120, 165	216, 240, 262	442
BaOX5	–, 165	220, 240, 256	444
BaOX6	160, 176	222, 240, 260	442
BaOX7	–, 164	220, –, 254	448, 464
BaOX8	–, 164	220, –, 254	460
BaOX9	–, 165	222, –, 256	452
BaOX10	–, 154	220, –, 244	444
BaOX11	–, 160	220, 238, 256	454
BaOX12	–, 164	232, –, 248	460, 508
BaOX13			

TABLE 6

The starting and ending temperatures of each of the weight losses from the TG results on the various oxalates examined

Sample	Loss of water	Loss of oxalic acid	Loss of CO
BaOX1	160–240	240–280	420–480
BaOX2	80–174	200–244	400–520
BaOX3	80–180	205–268	440–520
BaOX4	80–180	200–270	431–540
BaOX5	80–180	200–274	440–520
BaOX6	80–180	200–275	420–522
BaOX7	80–170	200–280	420–531
BaOX8	80–178	200–274	420–530
BaOX9	80–190	200–264	430–520
BaOX10	80–190	200–270	410–520
BaOX11	80–190	200–270	420–525
BaOX12	80–190	200–270	429–534
BaOX13	100–193	–	457–560

The DTA and TG curves for the samples prepared as described gave the following results. The oxalates prepared using free oxalic acid gave DTA and TG traces similar to those of the acid barium oxalates. The barium oxalate preparations in which a salt of oxalic acid was used gave DTA and TG curves similar to those for barium oxalate hemihydrate. To check if it was free oxalic acid which was required for the formation of the acid salt a sample of barium oxalate hemihydrate was soaked in oxalic acid solution. The resulting DTA and TG data were similar to those of the acid salt prepared using barium chloride and oxalic acid solutions. The TG curve for the barium oxalate compound prepared from 0.1 mol oxalic acid and 0.1 mol

TABLE 7

The starting and ending temperatures of the peaks for DTA

Sample	Loss of water	Loss of oxalic acid	Loss of CO	Phase change
BaOX1	160–220	256–280	344–484	800–820
BaOX2	80–172	200–280	360–476	
BaOX3	80–180	180–280	400–520	
BaOX4	80–180	180–272	360–580	
BaOX5	144–180	180–260	380–520	
BaOX6	154–180	180–272	380–520	
BaOX7	120–180	200–272	380–520	
BaOX8	120–180	180–260	380–520	
BaOX9	120–180	208–272	360–492	
BaOX10	100–180	180–264	360–480	
BaOX11	80–160	160–260	380–500	
BaOX12	120–200	200–280	380–540	
BaOX13	90–200	–	440–520	780–820

barium chloride showed no indication of any oxalic acid in the molecule but the resulting peak for the loss of carbon monoxide has become complex.

It is concluded that the DTA and TG curves of the acid barium oxalate compounds showed four peaks and three weight-loss regions. The DTA traces for some of the compounds showed that the carbon monoxide peak does not seem to be a simple one stage reaction (in particular samples BaOX1, BaOX7 and BaOX12). On lowering the concentration of the starting material in the DTA experiments the complexity of the carbon monoxide loss becomes more apparent. The TG results agree very well with those obtained by chemical analysis.

The results obtained show that in the preparation of a barium oxalate compound, using barium chloride and oxalic acid as starting materials, the product could not be $BaC_2O_4 \cdot \frac{1}{2} H_2O$. If the compound formed had been the normal oxalate of barium then the percentage of oxalate should be about 38% and barium 58% giving a water content of 4%. From the results shown, the barium content of the prepared samples was approximately 40%, the oxalate was 51% giving a water content of 9%.

These results are consistent with a molecular weight of $(342.25)_n$, where n is a whole number. On the basis that $n = 1$ and the fact that the compound $BaC_2O_4 \cdot \frac{1}{2} H_2O$ has a molecular weight of 234.3 this results in a difference of 109 between the two molecular weights.

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