

The thermal decomposition of beryllium oxalate and related materials

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Abstract

The compound beryllium oxalate trihydrate decomposes on heat treatment to beryllium oxide. Preparation of samples of beryllium oxalate under varying conditions revealed that the oxalate is hygroscopic and can exist as a trihydrate, a monohydrate or a combination of both depending on the partial pressure of water vapor above the sample. The dehydration of these samples was shown by the thermogravimetric data to be followed by a subsequent one-step decomposition to BeO. There was some indication of intermediate compounds existing in the decomposition to the BeO. The kinetic behavior of this latter stage was studied in a series of isothermal experiments and was best described by a D2 diffusion mechanism with an activation energy of 88.9 kJ mol^{-1} . This is lower than that commonly reported for other Group II oxalates which suggests a less stable oxalate. By decomposing the beryllium oxalates at various temperatures, the surface area of the solid residue increases with a loss of crystal morphology but the oxide product resists sintering. © 1998 Elsevier Science B.V.

1. Introduction

In this study the thermal decomposition of beryllium oxalate is investigated using thermogravimetry (TGA) and differential thermal analysis (DTA). A brief report of related beryllium compounds such as beryllium hydroxide, beryllium sulfate and basic beryllium carbonate is also included. To properly understand the behavior of these compounds it should be noted that beryllium is the first member of the alkaline earth metals. As such, similarities in its chemistry can be made with other alkaline earth members, particularly magnesium and calcium. However, as usual a diagonal relationship can be drawn showing relationships in the properties of beryllium compounds with those of aluminum. Thermal studies on calcium and

magnesium salts are numerous but corresponding studies on beryllium are less well documented [1].

Calcium oxalate occurs associated with one or two molecules of water, and thermal decomposition involves clear stages involving loss of water, decomposition of the anhydrous oxalate to the carbonate and finally decomposition of the carbonate to the oxide [2]. Magnesium oxalate shows a separate stage of dehydration, but the anhydrous material decomposes directly to the oxide [3]. It is shown here that the hydrated state of beryllium oxalate depends on the gaseous environment and preparative conditions. In this the diagonal relationship to aluminum is apparent, for the precipitate obtained from oxalic acid and aluminum salt solutions gives material of indeterminate composition probably best described as a basic oxalate [4]. On the other hand, beryllium hydroxide is well characterized and compares well with calcium hydroxide and magnesium hydroxide as opposed to

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aluminum hydroxide where the precipitate is generally ill-defined [5,6]. Beryllium sulfate is most commonly encountered in the tetrahydrate form, and is more soluble than other alkaline earth sulfates. However, the thermal stability of beryllium sulfate is less than that of other alkaline earth sulfates. The only hydrate intermediate confirmed on decomposition is the dihydrate [7]. At temperatures in the 500–600°C range the anhydrous beryllium sulfate begins to decompose by loss of SO₃-yielding BeO. Beryllium basic carbonate (approximate formula: BeCO₃·2Be(OH)₂) is usually regarded as an intermediate compound in the preparation of beryllium hydroxide [8]. As with other salts, the order of thermal decomposition of alkaline earth carbonates is



with barium carbonate decomposing only above 1000°C [9]. Beryllium carbonate first loses water around 100°C, then at temperatures up to 300°C loses carbon dioxide to yield beryllium oxide. All of this information can be found in the review by Everest [1]. The thermal behavior of beryllium oxalate and the other oxysalts of beryllium described in the present study relates to the industrial preparation of the metal where these materials are involved as precursors or could be potential precursors in the extraction of beryllium from its ores [10].

2. Experimental

The techniques utilized in the present study included thermogravimetry (TG), differential thermal analysis (DTA), X-ray powder diffraction and scanning electron microscopy. The TG equipment was a Perkin Elmer TGSII unit. The runs were carried out in platinum pans under a dynamic atmosphere of nitrogen at a flow rate of 30–40 ml min⁻¹ at a heating rate of 10°C min⁻¹. In this and other experiments trace quantities of oxygen present in the nitrogen gas were eliminated by passing it through an oxiclear disposable gas purifier. Some isothermal experiments were also performed from which the kinetics of decomposition were determined. The DTA equipment used was a Perkin Elmer DTA 1700 system High Temperature DTA unit. The conditions for the heating runs were the same as those noted above for TG. The

surface areas were measured using a Quantasorb sorption system. X-ray powder diffraction studies were performed using a General Electric XRD600. A JOEL JSM-6100 scanning electron microscope was also used to study surface morphology.

3. Results and discussion

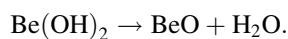
The procedure in the preparation of the trihydrate of beryllium oxalate (BeC₂O₄·3H₂O) involved the preparation of Be(OH)₂, followed by conversion to beryllium basic carbonate and finally the preparation of the oxalate. The results and discussion are therefore arranged in that order.

3.1. Characterization of beryllium sulfate (BeSO₄·4H₂O)

This compound was the starting point for all the preparations described here leading to the preparation of beryllium oxalate. Beryllium sulfate originated from calcined BeO dissolved in sulfuric acid. TG analysis given in Fig. 1 shows a two-stage dehydration between 100 and 300°C. This is followed by breakdown of the anhydrous sulfate above 620°C to BeO.

3.2. Preparation and characterization of Be(OH)₂

Be(OH)₂ was prepared by passing air over concentrated ammonium hydroxide and bubbling the gas into a beryllium sulfate solution. Beryllium hydroxide was precipitated. When the pH of the solution reached 7–8, bubbling was terminated. The slurry was filtered. Beryllium hydroxide was washed with water and then oven-dried. To eliminate ammonium sulfate trapped in the product, the dried product was crushed, ground and repulped in water at ambient temperature. The solids were again dried at 100°C. The cycle was repeated twice. The TG plot of beryllium hydroxide is shown in Fig. 2 as a single-step dehydroxylation, starting at around 280°C,



Everest [1] cites complete conversion to BeO at temperatures greater than 950°C, but this is not apparent from the TG data.

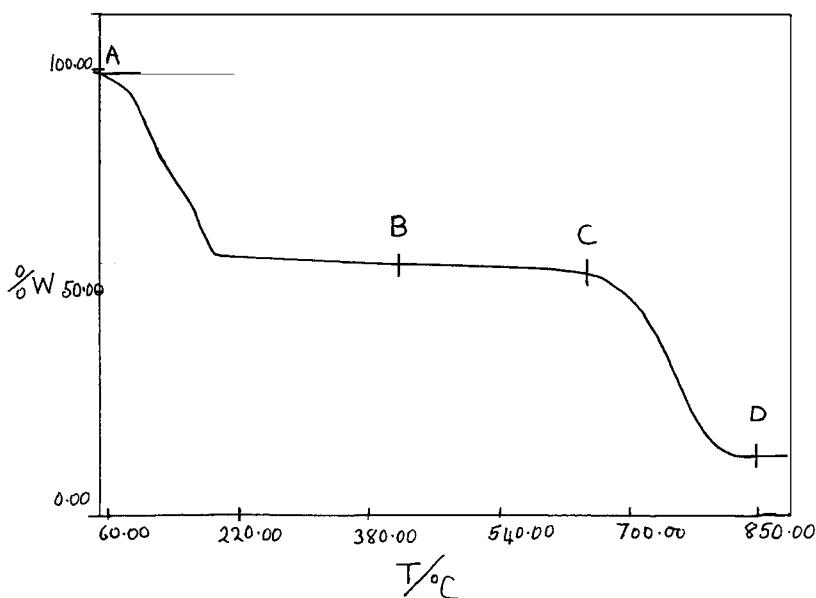


Fig. 1. TG analysis of beryllium sulfate. Plot of % weight (%w) against temperature (T). Point A, 99.55 %W; Point B, 56.42 %W; Point C, 54.5 %W; Point D, 14.02%.

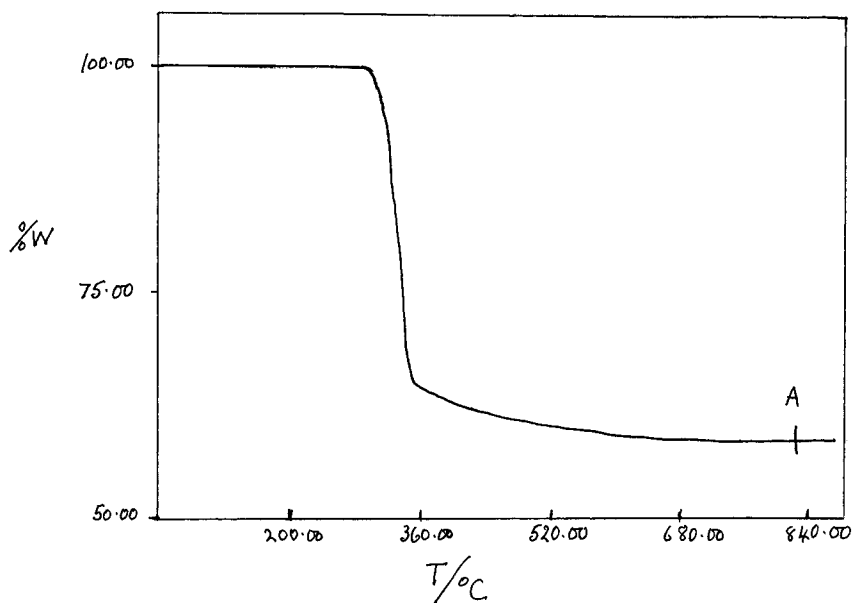


Fig. 2. TG analysis of beryllium hydroxide. Plot of % weight (%w) against temperature (T). Point A, 53.38%.

3.3. Preparation and characterization of $\text{Be}(\text{OH})_2 \cdot 2\text{BeCO}_3$

The next stage in the preparation of the oxalate was the production of basic beryllium carbonate. Beryl-

lium hydroxide was dissolved in ammonium carbonate solution. This process was slow and took several days (at 50°C) for complete dissolution. Once dissolved the solution was steam-hydrolyzed. Basic beryllium carbonate was precipitated, filtered off and

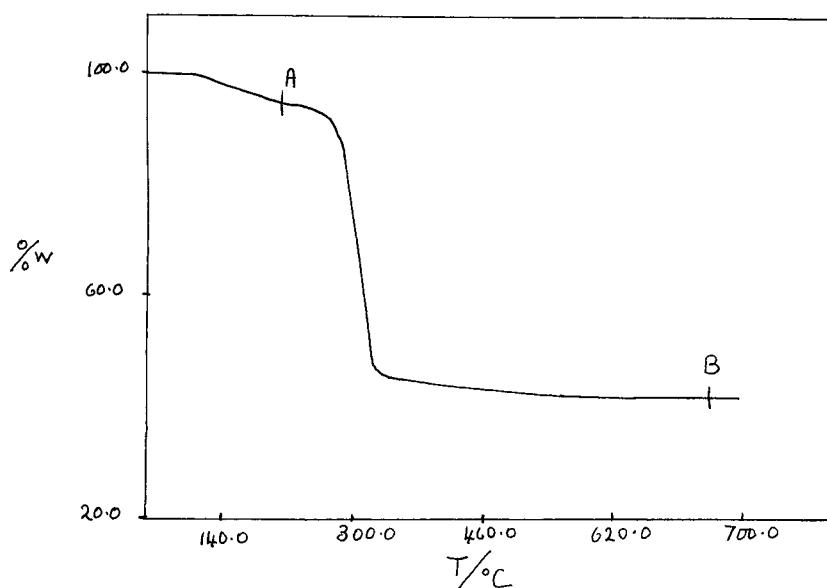
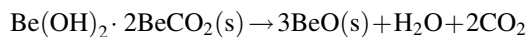


Fig. 3. TG analysis of basic beryllium carbonate. Plot of % weight (%w) against temperature (T). Point A, 94.03%; Point B, 41.82%.

recovered (dried at 110°C). TG analysis of the basic beryllium carbonate in air (Fig. 3) confirmed the formula and demonstrated a single stage decomposition (in the temperature range 180–350°C)



3.4. Preparation and characterization of beryllium oxalate

To prepare the beryllium oxalate samples basic beryllium carbonate was dissolved in a slight excess of oxalic acid solution. The solution was evaporated at a temperature of 55°C and beryllium oxalate crystals were obtained. Unlike many other oxalates, beryllium oxalate is quite soluble in water. When the product

was air-dried, the TG plot (Fig. 4) showed that the sample had a formula $\text{BeC}_2\text{O}_4 \cdot 1.8\text{H}_2\text{O}$. When this product was left standing over water in a sealed desiccator, it continued to absorb moisture and did not achieve a constant weight after 9 days. At this time a TG analysis (Fig. 5) indicated a formula for the product of $\text{BeC}_2\text{O}_4 \cdot 3.5\text{H}_2\text{O}$. In order to obtain the desired trihydrate the compound was placed in sealed desiccators over four different saturated salt solutions as noted in Table 1 [11]. The results of these experiments are noted in Table 2. The NH_4Cl saturated solution atmosphere gave the only constant oxalate product weight after 8 days. The $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ and the $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ were visibly seen not to be satisfactory. Both these salt solutions dehydrated the oxalate product until it was hard, like plaster. The $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$

Table 1
Solubility/vapor pressure data on selected saturated salt solutions

Temperature	Compound	Vapor pressure	Solubility
25°C	H_2O	23.756 mm Hg	Free H_2O at 25°C
24.5°C	$\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$	7.08 mm Hg	279 g/100 cc at 0°C
24.5°C	$\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	11.6 mm Hg	266 g/100 cc at 0°C
25°C	NH_4Cl	18.6 mm Hg	29.7 g/100 cc at 0°C
24.5°C	$\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$	20.1 mm Hg	58.7 g/100 cc at 1000°C

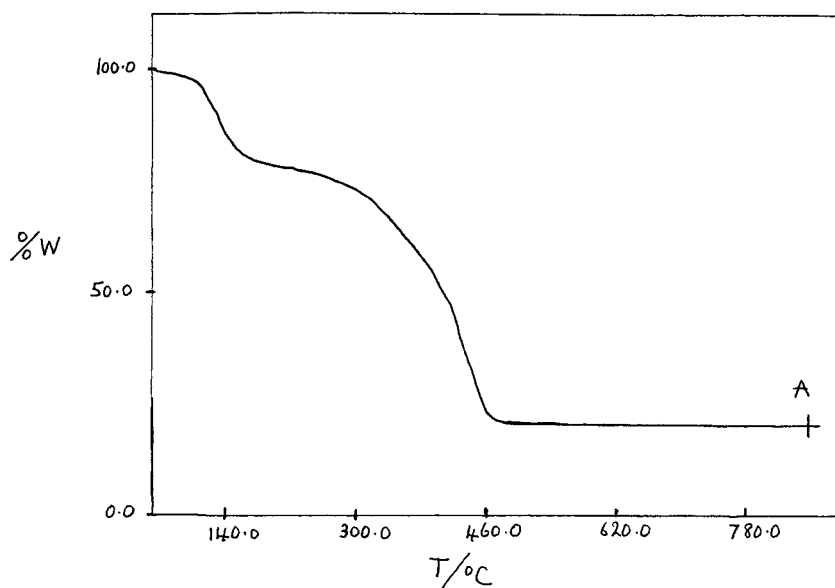


Fig. 4. TG analysis of beryllium oxalate with a stoichiometric composition $\text{BeC}_2\text{O}_4 \cdot 1.8\text{H}_2\text{O}$. Plot of % weight (% w) against temperature (T). Point A, 19.3%.

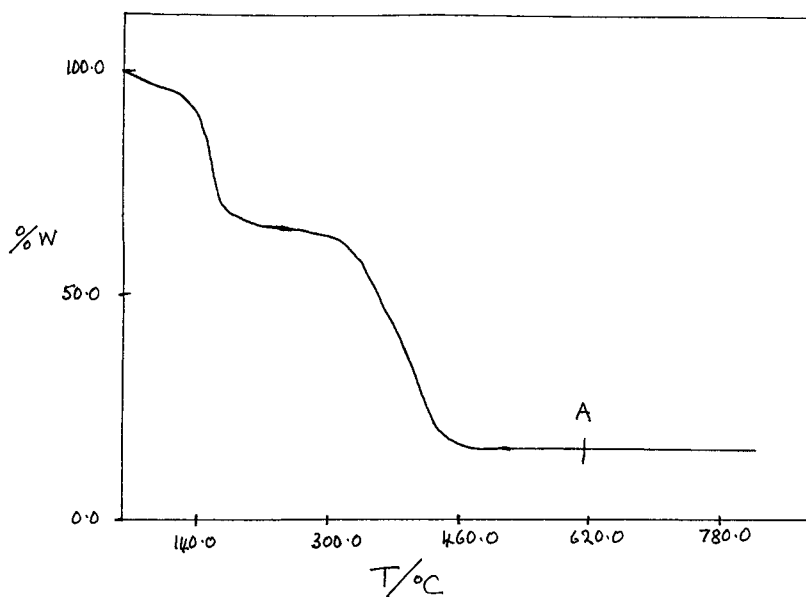


Fig. 5. TG analysis of beryllium oxalate with a stoichiometric composition $\text{BeC}_2\text{O}_4 \cdot 3.5\text{H}_2\text{O}$. Plot of % weight (% w) against temperature (T). Point A, 15.61%.

solution atmosphere provided a soupy substance which was still absorbing water after 8 days. This was similar to the behavior of the product when it was placed over free standing water. TG analysis was done

on the NH_4Cl (Fig. 6), $\text{CaCl}_2 \cdot \text{H}_2\text{O}$ (Fig. 7), and the $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (Fig. 8) saturated solution atmosphere products. The TG run on the NH_4Cl saturated solution product was run on day 8 when a constant mass had

Table 2
Data from saturated salt solution atmosphere for $\text{BeC}_2\text{O}_4 \cdot \text{XH}_2\text{O}$

Day	Salt	Product weight (g)	Observations
1	$\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$	1.754	
2		1.4881	Product dry
5		1.4632	Very dry
6		1.4657	
7		1.4667	Powder
8		1.4704	
16		–	a
1		$\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	6.3970
2	5.7484		
5	5.4563		Dry product
6	5.4442		
7	5.4379		
8	5.4255		
19	–		b
1	NH_4Cl		2.881
2		2.7520	
5		2.6781	
6		2.6853	
7		2.6878	
		2.6867	c
1	$\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$	3.7806	
2		3.9090	Product soupy
5		4.2410	
6		4.3215	Free standing
7		4.3710	Liquor
8		4.4177	d

^aProduct was solid-cemented to the evaporating dish. TG analysis showed the compound to be $\text{BeC}_2\text{O}_4 \cdot 1.3\text{H}_2\text{O}$.

^bProduct was cemented to the dish. TG analysis indicated $\text{BeC}_2\text{O}_4 \cdot 2.1\text{H}_2\text{O}$.

^cTG analysis indicated the trihydrate $\text{BeC}_2\text{O}_4 \cdot 3\text{H}_2\text{O}$.

^dTG analysis was not run.

been obtained. This product corresponded to the trihydrate $\text{BeC}_2\text{O}_4 \cdot 3\text{H}_2\text{O}$. TG analysis yielded the formula for the sample held over $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ to be $\text{BeC}_2\text{O}_4 \cdot 1.3\text{H}_2\text{O}$ and that over $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ to be $\text{BeC}_2\text{O}_4 \cdot 2.1\text{H}_2\text{O}$.

All TG data showed a change from around 250 to 480°C with an end product of the oxide BeO. The difficulty is identifying the 'sloping plateau' preceding the decomposition to the oxide. In Fig. 4, for the air-dried crystals, the plateau would seem to correspond to the anhydrous product (theoretical residue

for BeC_2O_4 is 74.9%, whilst for the monohydrate theoretical residue is 88.8%), and the overall thermal treatment shows dehydration followed by decomposition to the oxide. Fig. 5 shows the TG of the oxalate which had been allowed to absorb water from the air, with a nominal formula of $\text{BeC}_2\text{O}_4 \cdot 3.5\text{H}_2\text{O}$ which simply shows an increase in water content and a decomposition range from 300 to 480°C where the oxalate decomposes to the oxide in a single step. If the decomposition was from the anhydrous oxalate, the plateau would be at 60.6%, but the direct decomposition from the monohydrate would be from a plateau of 71.8% and cannot be excluded as a possibility, due to the sloping character of the plateau. The material labelled as having the stoichiometric formula $\text{BeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, produces a similar two-stage process (Fig. 6) where the residue for the BeC_2O_4 would be 63.2% and that for $\text{BeC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ would be 75.0%, and this also does not resolve the problem as to whether the degradation is from the monohydrate or the anhydrous oxalate. The materials left to equilibrate over saturated CaCl_2 and saturated $\text{Ca}(\text{NO}_3)_2$ solutions produced a new feature, namely, a decomposition in the region from 220 to 300°C immediately preceding the degradation stage (300–480°C) to the oxide (see Figs. 7 and 8). If both these stages are regarded as a breakdown via an unstable intermediate, possibly a carbonate to the oxide, then it again leaves the problem unresolved as to whether the decomposition is from the monohydrate or the anhydrous oxalate.

The residue at 300°C could be prepared on a larger scale of a few grams and identified by X-ray powder diffraction. The residue from the trihydrate (see Fig. 6) and from the samples prepared over CaCl_2 saturated solution and from those prepared over $\text{Ca}(\text{NO}_3)_2$ solution and then both heated to 300°C all showed beryllium oxalate monohydrate as the main phase present in X-ray powder diffraction analysis. In some cases the trihydrate was also detected in small quantities. This could be attributed to the hygroscopic nature of the samples, and the presence of the oxide also detected emphasizes the difficulty of reproducing thermal analysis data on a somewhat larger scale. In all the X-ray diffraction data obtained there was no sign of any intermediate product such as possibly indicated in Figs. 7 and 8.

An examination of the single stage decomposition of a prepared sample corresponding to the formula

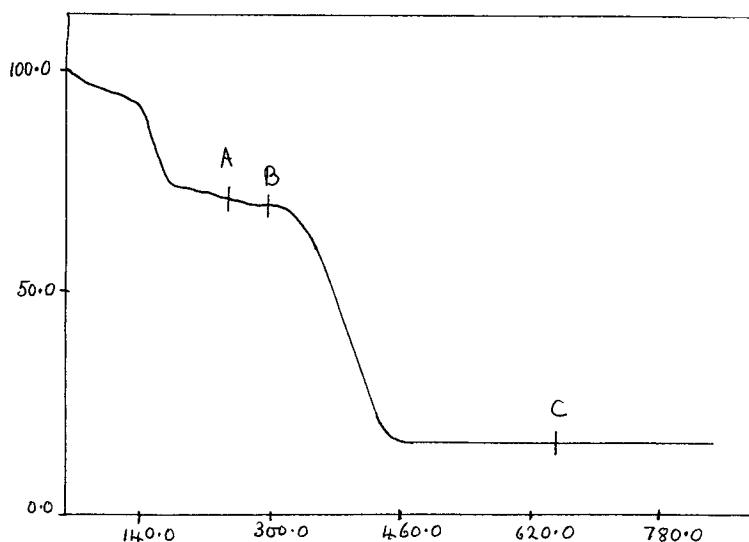


Fig. 6. TG analysis of beryllium oxalate equilibrated over NH_4Cl saturated solution, $\text{BeC}_2\text{O}_4 \cdot 3\text{H}_2\text{O}$. Plot of % weight (% w) against temperature (T). Point A, 70.41%; Point B, 69.1%; Point C, 16.37%.

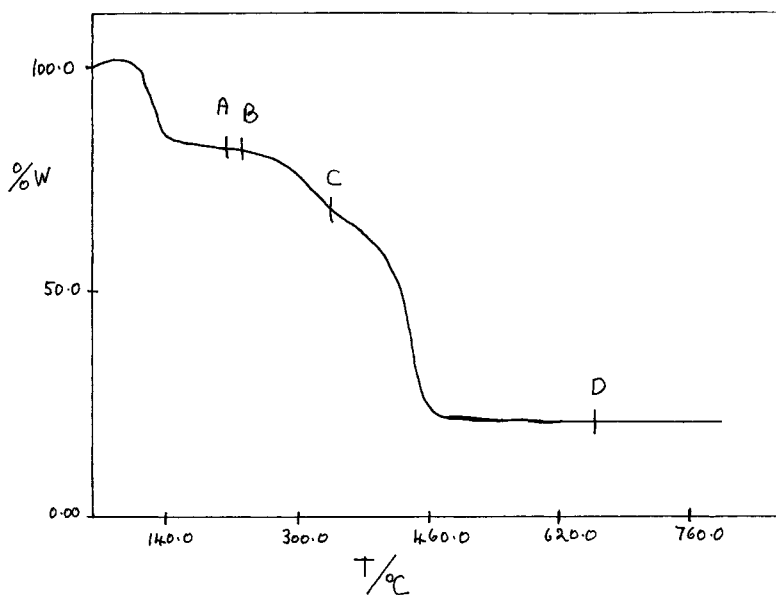


Fig. 7. TG analysis of beryllium oxalate equilibrated over CaCl_2 saturated salt solution, $\text{BeC}_2\text{O}_4 \cdot 1.3\text{H}_2\text{O}$. Plot of % weight (% w) against temperature (T). Point A, 82.12%; Point B, 81.8%; Point C, 68.39%; Point D, 20.69%.

$\text{BeC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ by an isothermal technique (at six temperatures from 380 to 430°C) showed a best fit for Arrhenius plots based on a D2 mechanism with an Activation Energy of 89 kJ mol^{-1} .

A sample of the trihydrate was heated at 350°C in air for up to 220 min, and the surface area was determined. It can be seen from Table 3 that the decomposition of the oxalate produced an increase

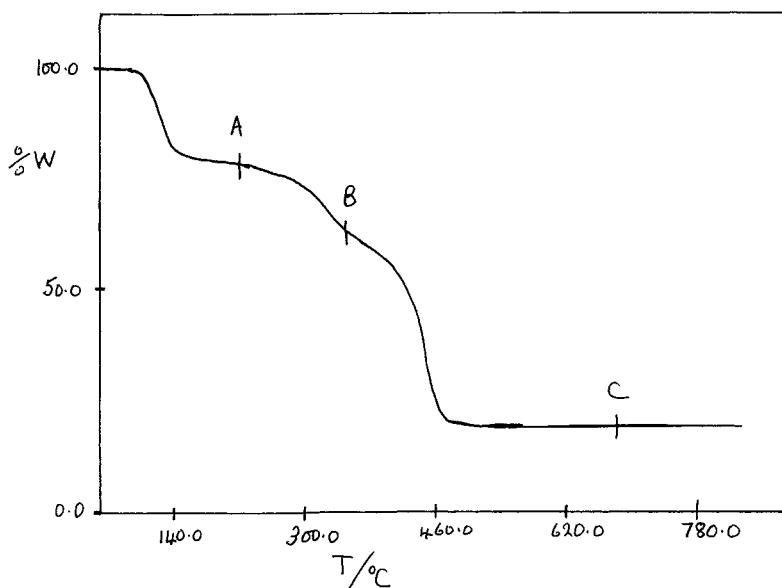


Fig. 8. TG analysis of beryllium oxalate equilibrated over $\text{Ca}(\text{NO}_3)_2$ saturated solution, $\text{BeC}_2\text{O}_4 \cdot 2.1\text{H}_2\text{O}$. Plot of % weight (%w) against temperature (T). Point A, 78.02%; Point B, 62.71%; Point C, 18.5%.

Table 3

Variation of the surface area of the oxalate upon heating in air at 350°

Time of heating/min	Phases present
25	Beryllium oxalate and beryllium oxide
50	
75	
105	Beryllium oxide
130	
160	
190	
220	

Table 4

Surface area of samples heated for 1/2 h at various temperatures in air

Temperature ($^\circ\text{C}$)	Surface area ($\text{m}^2 \text{g}^{-1}$)
150	4.03
200	6.31
250	9.11
300	1.63
350	88.79
400	358.24
450	471.59
500	244.86

in the surface area, but once formed the product residue BeO was resistant to sintering. The scanning electron microscope studies of these samples showed a lack of crystalline morphology on samples heated for 25 min, but samples heated for longer periods indicated the development of a crystalline structure in the samples identified as BeO . Surface area measurements were also made on samples heated for 30 min at various temperatures (see Table 4). It can be seen that the thermal decomposition of the oxalate between 300 and 400°C produces an oxide of high surface area resistant to sintering. The small size of the beryllium

atom would lead one to expect that the oxide would resist sintering.

All samples were subjected to DTA study. This showed that all dehydrations and dehydroxylation were endothermic. The decomposition of BeSO_4 at 600°C was also endothermic, as was the degradation of the carbonate to the oxide at around 270°C . The DTA plots for the oxalate showed overlapping endothermic peaks lending some substance to the interpretation of the degradation of the oxalate samples going through an intermediate stage.

4. Conclusions

In this study beryllium oxalate is shown to be a hygroscopic material which exists as either a trihydrate, monohydrate or a combination of both in prevailing ambient conditions. Decomposition occurs first by loss of water, but the final decomposition stage to the oxide is probably from the monohydrate rather than the anhydrous oxalate. There is some indication of an intermediate material being formed in the decomposition, but the TG indication of such a stage is obscured by the conditions of preparation of the samples and the hygroscopic nature of beryllium oxalate. On a sample of the monohydrate the single-step decomposition was described by decelerating mechanisms, best fitted by the D2 diffusion mechanism with an activation energy of 88.9 kJ mol^{-1} . This value is somewhat lower than that found for other Group II oxalates which would suggest a less stable oxalate. Surface area determinations on heat-treated samples showed an increase in surface area upon formation of BeO, but the oxide was highly resistant to sintering. The scanning electron microscopy photo-

graphs showed a loss of crystalline morphology during the decomposition process.

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