

## BORON COMPOUNDS OF OXALIC ACID.

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## INTRODUCTION.

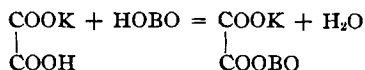
In 1702, Homberg<sup>1</sup> isolated boric acid, which he named "sal sedativum" because of its medicinal properties. In the literature since that time there are many references to the use of boric acid and its compounds as sedatives, especially in the treatment of epilepsy; there has been, however, much difference of opinion as to their value. In 1920, Pierre Marie<sup>2</sup> and his co-workers found that potassium borotartrate could be used with considerable success in controlling the convulsions associated with epilepsy.

This laboratory has been engaged for some time in a rather comprehensive study of the preparation and properties of this potassium salt and related substances, with the end in view, firstly, of discovering other compounds even better suited to the purpose, and, secondly, of arriving at knowledge respecting their true constitution.

There has long been a difference of opinion as to the structure of tartar emetic and similar compounds, some chemists believing the antimony (arsenic, boron) to be on the carboxyl group of the tartaric acid, while others have held that the product was formed by reaction of an oxide or acid of the metalloid in question with an hydroxyl group. We were, therefore, interested in preparing compounds in which we were sure of the position of the boryl group and in comparing the properties of these compounds with those of doubtful structure.

In this paper we record the results of attempts to prepare boron compounds of oxalic acid.

It was stated by Duve,<sup>3</sup> in 1869, that boric acid does not combine with oxalic acid. Several years later, Magnanini<sup>4</sup> showed that the electrical conductivity of aqueous solutions of  $\alpha$ -hydroxy acids, such as lactic or tartaric, was increased markedly when boric acid was added. He attributed this result to the formation of strongly acid compounds by union of the boric acid with the hydroxy acid. No such increase in conductivity occurred in the case of oxalic acid and it was assumed that in this instance there was no tendency for combination. This conclusion was attested to by Adam,<sup>5</sup> who reported that neither oxalic acid nor its salts combine with boric acid. Werner,<sup>6</sup> while agreeing with the above statements as far as oxalic acid itself is concerned, succeeded in preparing what he thought to be potassium boro-oxalate by boiling a water solution of potassium hydrogen oxalate and boric acid. He considered the compound to have been formed according to the following equation:



It separated from solution with water of crystallization, the analytical figures

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indicating the formula  $(\text{COOK}-\text{COOBO})_2\cdot 3\text{H}_2\text{O}$ . The compound is thus described in textbooks.<sup>7</sup>

We have repeated this work and have isolated a compound agreeing in properties to that of Werner but differing somewhat in composition. It is believed the difference in analytical results is due to the fact that we have worked with a purer product than Werner had at his disposal. Microscopic examination of material prepared according to Werner's directions showed it to be composed of two types of crystals.

We have also been able to isolate an analogous and hitherto unknown compound of oxalic and boric acids.

From this experience with these substances we are inclined to disagree with Werner as to the ester-like structure which he has assigned to the so-called potassium boro-oxalate. We feel it more in keeping with the facts to consider this substance, and the free acid corresponding, as double salts. The formulas proposed for these compounds are  $\text{KHC}_2\text{O}_4\cdot\text{HBO}_2\cdot\text{H}_2\text{O}$  and  $\text{H}_2\text{C}_2\text{O}_4\cdot\text{HBO}_2\cdot 3\text{H}_2\text{O}$ , or, what is substantially the same thing, namely,  $\text{KHC}_2\text{O}_4\cdot\text{H}_3\text{BO}_3$  and  $\text{H}_2\text{C}_2\text{O}_4\cdot\text{H}_3\text{BO}_3\cdot 2\text{H}_2\text{O}$ .

#### EXPERIMENTAL PART.

*Potassium Boro-oxalate.*—Molecular proportions of ortho-boric acid and potassium hydrogen oxalate were boiled in water solution for one-half hour. On cooling, a mixture of potassium hydrogen oxalate and the boro-oxalate crystallized. The first-mentioned compound is less soluble than the second, and in subsequent experiments the solution was filtered at about  $70^\circ$ , or after crystals of potassium hydrogen oxalate had appeared. In this way most of this substance was removed. The boro-oxalate separating from the filtrate on cooling was recrystallized six times from water. Microscopic examination of the material proved it to be made up of groups of small transparent monoclinic crystals. No other type of crystals could be recognized. It was dried over sulphuric acid and analyzed.

*C and H.*

0.2275, 0.2030 Gm. substance: 0.1058, 0.0945 Gm.  $\text{CO}_2$  and 0.0462, 0.0406 Gm.  $\text{H}_2\text{O}$ .  
 $\text{C}_2\text{H}_4\text{O}_7\text{BK}$ . Calculated, C 12.62, H 2.12. Found, C 12.68, H 2.27,  
 12.69 2.23

$\text{B}_2\text{O}_3$ .\*

0.5264, 0.5344 Gm. substance: 13.42, 13.73 cc. 0.1 N NaOH.  
 $\text{C}_2\text{H}_4\text{O}_7\text{BK}$ . Calculated,  $\text{B}_2\text{O}_3$  18.29. Found,  $\text{B}_2\text{O}_3$  18.22, 18.36.

$\text{C}_2\text{O}_4$ .

0.4405, 0.3144 Gm. substance: 46.40, 33.17 cc. 0.1 N  $\text{KMnO}_4$ .  
 $\text{C}_2\text{H}_4\text{O}_7\text{BK}$ . Calculated,  $\text{C}_2\text{O}_4$  46.27. Found,  $\text{C}_2\text{O}_4$  46.34, 46.42.

$\text{H}_2\text{O}$ .

The formulas  $\text{COOK}\cdot\text{COOBO}\cdot 2\text{H}_2\text{O}$  and  $\text{COOK}\cdot\text{COOH}\cdot\text{HBO}_2\cdot\text{H}_2\text{O}$  correspond to the analytical figures for carbon, hydrogen, boron and oxalate and should lose two molecules of water, or 18.95%, if completely dehydrated. Heating in an oven at  $120^\circ$  failed to cause a loss of weight corresponding to two molecules of water. At  $140-150^\circ$  for sixty hours a sample of 1.6728 grams lost 0.3162, or 18.90 per cent. The residual material, on analysis, proved to have retained a small amount of its hydrogen and to be too low in carbon. In other words, it was de-

\* Boron was determined by heating the substance in a platinum crucible in the presence of an excess of potassium carbonate until all organic matter was oxidized. From this point the procedure was essentially that outlined by Wherry and Chapin.<sup>8</sup>

composed by heat before losing completely the elements of water. We consider the very gradual loss of weight as corresponding, for the most part, to the dehydration of metaboric acid to form pyroboric acid. It is well known that this change takes place very slowly at this temperature.

Potassium boro-oxalate is soluble in water and insoluble in the common organic solvents. It is possible, however, to completely remove the boron in the compound by stirring for some time with cold 95% alcohol. The material remaining insoluble was analyzed and found to be potassium hydrogen oxalate.

The substance titrates as a dibasic acid. Using phenolphthalein as indicator, a little more than half the theoretical amount of standard NaOH is required to give an end-point. On addition of mannite, the solution again becomes acid, the amount of alkali required for complete neutralization corresponding closely to the calculated amount. This behavior, as well as the alcohol extraction and very gradual loss on heating, agrees well with the assumption that the substance is a double salt.

Werner reports that there is no immediate precipitation when barium chloride is added to a cold, strong solution of potassium boro-oxalate, but that a precipitate rapidly forms on warming. We have found that no precipitation takes place at once, in the cold, but that, after a short time, solid does separate from solution and without the aid of heat. This fact cannot be taken as evidence for an ester structure, as a similar time interval has been observed between the addition of a barium chloride solution to a concentrated solution of sodium or potassium hydrogen oxalate and the precipitation of barium oxalate.

*Boro-oxalic Acid.*—This substance was prepared by dissolving 207 grams of oxalic acid and 104 grams of boric acid in 300 cc. of water and gently boiling for thirty minutes. The solution was cooled in an ice-bath, the crystals filtered off and dried by suction. They were recrystallized seven times from water and dried over calcium chloride. Under the microscope, but one type of crystals could be recognized, these being long, slender, transparent hexagonal prisms, melting at 90°. The material was analyzed with the following results:

*C and H.*

0.3095 Gm. substance: 0.1434 Gm. CO<sub>2</sub> and 0.1370 Gm. H<sub>2</sub>O.  
C<sub>2</sub>H<sub>3</sub>O<sub>3</sub>B. Calculated, C 12.75, H 4.78. Found, C 12.63, H 4.95.

*B<sub>2</sub>O<sub>3</sub>.*

0.5424, 0.5134 Gm. substance: 29.09, 27.55 cc. 0.1 N NaOH.  
C<sub>2</sub>H<sub>3</sub>O<sub>3</sub>B. Calculated, B<sub>2</sub>O<sub>3</sub> 18.61. Found, B<sub>2</sub>O<sub>3</sub> 18.73, 18.78.

*C<sub>2</sub>O<sub>4</sub>.*

0.4018, 0.5094 Gm. substance: 42.06, 53.73 cc. 0.1 N KMnO<sub>4</sub>.  
C<sub>2</sub>H<sub>3</sub>O<sub>3</sub>B. Calculated, C<sub>2</sub>O<sub>4</sub> 46.78. Found, C<sub>2</sub>O<sub>4</sub> 46.40, 46.43.

*H<sub>2</sub>O.*

On being heated to 100–110°, boro-oxalic acid loses weight beyond the loss required to correspond to 4H<sub>2</sub>O, which we attribute to loss of oxalic acid. This is confirmed by the fact that the residual material analyzes too low for carbon and too high for boron in COOH.CO<sub>2</sub>H.HBO<sub>2</sub> or COOH.CO<sub>2</sub>BO. This behavior accords better for the double salt formula COOH.CO<sub>2</sub>H.HBO<sub>2</sub>.3H<sub>2</sub>O than for the ester formula COOH.CO<sub>2</sub>BO.4H<sub>2</sub>O.

When barium chloride is added to a saturated solution of this compound in water, there is no precipitation for some time. However, after standing a while, a heavy precipitate appears. This is exactly the behavior we have observed where BaCl<sub>2</sub> is added to a strong solution of oxalic acid.

In the presence of mannite the compound titrates as a tri-basic acid.

*Di-potassium Boro-oxalate*.—Evidence of compound formation was obtained when di-potassium oxalate was heated with ortho-boric acid under the conditions described above. The product upon careful examination appeared to be homogeneous so far as crystalline form was concerned. On being heated at 110–120° for many hours, no loss of weight occurred as would have been the case had the material been merely a mixture of the original components, due both to loss of water of crystallization on the part of the potassium oxalate and the change of ortho-boric to meta-boric acid.

Several analyses were made and results were obtained indicating a formula,  $K_2C_2O_4 \cdot HBO_3$ . On repeated recrystallizations the analytical figures varied to such an extent that the study of the substance was discontinued as not being justified by its interest or importance to the problem in hand.

#### SUMMARY.

1. A compound has been prepared from potassium hydrogen oxalate and boric acid, and has been found to possess a different composition than that previously recorded in the literature.

2. A compound of boric acid and oxalic acid ( $H_2C_2O_4 \cdot H_3BO_3 \cdot 2H_2O$ ) hitherto undescribed has been isolated and analyzed.

3. There appears to be no evidence to justify assigning an ester structure to these compounds.

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APRIL 14, 1924.

#### CALCIUM SULPHIDE AS A CHEMICAL ANTIDOTE IN POISONING BY MERCURIC CHLORIDE.

In the *Journal of Laboratory and Clinical Medicine*, in 1917, a recovery was reported of mercuric chloride poisoning, following the administration of calcium sulphide as an antidote. In a more recent paper a number of cases of successful treatment were reported—to the extent that the statement is made in this paper (January 1923, *Hospital Corps Supplement to the U. S. Naval Medical Bulletin*) that "cases so treated (by mouth or intravenously) usually show an uneventful

recovery." Experiments with rabbits reported in the aforementioned publication, for May, by Lt. J. M. McCants, are not so encouraging; in fact, an amount equal to that employed as antidote of calcium sulphide produced death and, also, rabbits actually given mercuric chloride and then the antidote died more quickly than those only given the mercuric chloride. The author suggests that method of treatment may be at fault, possibly the purity of the sulphide. The experiments, however, indicate that further investigation is necessary to establish a reasonable reliability for the calcium sulphide treatment.