6. The presence of a primary alcohol group exerts a protective action over formic acid in the presence of hydrogen peroxide and any of the catalysts studied, making the rate of oxidation of such an acid as formic or acetic, much slower than in the absence of the alcohol.

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[CONTRIBUTION FROM THE LABORATORY OF GENERAL CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

THE PREPARATION OF BORIC ACID ANHYDRIDE AND ITS EFFICIENCY AS A DRYING AGENT

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Boric acid anhydride has been used by Schlesinger in the preparation of pure, dry formic acid[1] and also in the preparation of dry ether.[2] Since this substance is so efficient as a drying agent, it was of interest to determine the conditions which yield a product of maximum drying efficiency.

Preparation of Boric Acid Anhydride.—Fifty grams of pure boric acid crystals were placed in a 100-cc. platinum dish and heated over a Méker burner to a temperature of about 600°, a process attended by considerable frothing and the evolution of water vapor. The dish containing the clear, viscous liquid was then placed in an electrically heated muffle furnace and different samples were dehydrated at various temperatures for about an hour. At the end of this time, the dish was removed and the contents poured on a marble slab, where it immediately hardened to a clear glass. Although the boric acid melts at 577° a temperature of 800° is necessary for sufficient fluidity to permit easy pouring. Samples of the anhydride were dehydrated at 800, 900 and 1000°.

The glassy boric anhydride is extremely hard and is best ground in a ball mill using flint pebbles. After grinding for three days a powder was obtained that passed through a 100-mesh sieve, 90% of it passing through a 160-mesh sieve. To help eliminate this prolonged grinding a sample of the anhydride was prepared at 900° and the molten glass poured into purified carbon tetrachloride that had been chilled to 0°. This yielded material in the shape of small pellets which could be much more easily ground after evaporation of the carbon tetrachloride. Some of this preparation was used in the following tests.

In view of the fact that it has been stated that boric acid anhydride vaporizes at a red heat,[3,4] it should be possible to take advantage of this property for the preparation of this substance in a finely divided form and thus avoid the use of the ball mill. Preliminary experiments with this method were unsatisfactory. To effect volatilization in a current of dry air, a temperature of 1000° was necessary. The experiments were not continued because of the small yield and the fact to be shown later that boric acid prepared at high temperatures is not a satisfactory drying agent.

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[1] Schlesinger and Martin, THIS JOURNAL, **36**, 1589 (1914).

[2] Communication from Professor Schlesinger.

[3] Ebelmen, *Ann. chim. phys.*, **22**, 211 (1848).

[4] Tiede and Birnbräuer, *Z. anorg. Chem.*, **87**, 129 (1914).

Analysis of Ground Boric Oxide.—Since pulverizing in the ball mill introduced a certain amount of mineral matter, the boric acid was tested for purity by titration with alkali in the presence of glycerine.

The sample to be analyzed was first heated to practically constant weight at 600°. The amount of water given off under these conditions varied from 3.2 to 3.5% and is largely uncombined water. The anhydride present in the various samples was as follows.

Temperature at which sample was prepared	800°	900°	1000°	900° (Chilled in CCl_4)
Boric oxide, %	76.1	74.4	62.3	58.6

The Drying Efficiency of Boric Acid.—This was determined by passing air saturated with moisture through tubes of the anhydride. The apparatus used was similar to that described by Willard and Smith.[5] This permitted air to be passed through a flowmeter and saturated with moisture, after which it passed through a U-tube which contained the boric oxide. The tube was 18 cm. high with an inside diameter of 7 mm. It contained about 3 g. of boric oxide supported by cotton wool to prevent packing. The column of boric oxide was 7 mm. in diameter and 20 cm. long. This U-tube was followed by a weighed phosphorus pentoxide U-tube, the function of which was to show the amount of moisture that escaped absorption by the boric oxide.

Absorption Capacity.—Upon passing moist air over the boric oxide at a rate of 2 liters per hour, it was found that the boric oxide was efficient until moisture to the extent of about 28% of its weight had been absorbed. The change from the anhydride to the metaboric acid requires 25.8% of water. This reaction takes place rapidly,[6] while the change from meta to the ortho acid is comparatively slow, which indicates that the absorption of water vapor is attended primarily by the formation of the meta acid.

Induction Period.—Freshly ground boric oxide shows a reluctance to combine with moisture until a certain volume of the moist gas has been passed through the absorption tube. The following data show, moreover, that this volume is greater for the samples of boric acid prepared at higher temperatures.

Air saturated with water vapor at 23° was passed at a rate of 2 liters per hour over boric oxide which had been prepared at 800°. For the first two liters of air 0.0012 g. of moisture was unabsorbed; for 6 liters more the total unabsorbed moisture was 0.0018 g. With boric oxide prepared at 900° efficient absorption began only after 13 liters of air had been passed through the absorption tube, while with the 1000° preparation 21 liters was necessary. The boric oxide prepared by chilling the 900° preparation to 0° by pouring the melt into carbon tetrachloride required

[5] Willard and Smith, THIS JOURNAL, **44**, 2255 (1922).

[6] Meyers, *J. Chem. Soc.*, **111**, 172 (1917).

a passage of only 4 liters of dry air before it began to dry efficiently. Meyers[6] believes that when boric oxide is prepared at a temperature above 800°, molecular complexes are formed whose rate of reaction with water is much slower than the reaction of the boric oxide prepared at lower temperatures. The existence of such complexes would explain the "period of induction."

While an absolute comparison of the drying efficiency of the boric acid anhydride is difficult to make, these experiments indicate that this material is more efficient than sulfuric acid and calcium chloride but is somewhat inferior to phosphorus pentoxide and magnesium perchlorate.

With a drying column 40 cm. long and 7 mm. in diameter the boric oxide absorbed all the moisture from 88 liters of air saturated with moisture at 23° and flowing at the rate of 2 liters per hour.

Summary

1. In preparing boric oxide for drying purposes the boric acid should be dehydrated at about 800°. If prepared above this temperature, the product shows an induction period which decreases its efficiency.

2. The formation of a hard glass on cooling may be partly avoided by pouring the fused boric oxide into carbon tetrachloride at 0°. The resulting fragments are fairly easy to powder and the product is a very satisfactory drying agent.

3. The boric oxide was found to be an efficient drying agent until its moisture content rose to about 25% of its own weight.

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THE SYSTEM LITHIUM PERCHLORATE–WATER

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According to A. Potilitzin,[2] aqueous solutions of lithium perchlorate give the trihydrate, $LiClO_4 \cdot 3H_2O$, which loses approximately two-thirds of its combined water when heated between 98 and 100°, changing to monohydrate, and all of its water between 130 and 150°. The approximate nature of these data makes apparent the need of a more careful study of this system.

Preparation of Lithium Perchlorate

Anhydrous lithium perchlorate was made by the method of Richards and Willard.[3] The purity of the salt was proved by a modification of a

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[1] The results of this investigation were submitted by Clarence D. L. Ropp as partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Potilitzin, *J. Russ. Phys.-Chem. Soc.*, **19**, 339 (1887); **20**, 541 (1888).

[3] Richards and Willard, THIS JOURNAL, **32**, 4 (1910).