[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

The Reaction of Boron Fluoride with Water. I. Preparation and Some Properties of Pure Boron Fluoride Dihydrate[1]

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The preparation of a dihydrate of boron fluoride which is distillable without decomposition has been reported by Meerwein[4] and Meerwein and Pannwitz.[5] The extensive older literature, surveyed by these workers, indicates that considerable decomposition takes place on distilling solutions of varying concentrations of boron fluoride in water. Meerwein and Pannwitz,[5] however, reported that at pressures of about 1 mm. a pure product could be obtained by distillation of solutions of composition, $BF_3 \cdot 2H_2O$. Efforts in this Laboratory to prepare boron fluoride dihydrate of a high degree of purity by the procedure of Meerwein and Pannwitz,[5] for use in studies on the hydrolysis of boron fluoride, did not yield a product of constant boiling and melting points. A modification of the procedure, to yield a purer product, has been developed, and some studies have been made on the behavior of this compound on distillation and in solution in dioxane. The present paper reports the results of these studies.

Experimental

Preparation and Purification of Compounds.—Boron fluoride was prepared and purified by a standard procedure.[6] Boron fluoride dihydrate was prepared by passing 1 mole of boron fluoride into 2 moles of water cooled in an ice-bath. Absorption was slow at first but soon became rapid. When about 0.25 mole of gas had been dissolved, a considerable quantity of boric acid separated. Continued addition of boron fluoride caused the boric acid to go into solution. In some cases an excess of boron fluoride was absorbed and the calculated quantity of water added. The liquid thus obtained was used in subsequent studies.

Distillation Studies.—Fractional distillations of boron fluoride dihydrate were carried out with a Vigreux type column at pressures varying from 1 to 100 mm. Other distillations were done under a high vacuum in a closed system. A Sprengel pump[7] was used to maintain the vacuum and to collect any non-condensable gases formed by decomposition or chemical action on glass.

Melting Point Determinations.—Melting points of all fractions were determined in an all-glass apparatus, in which a mechanically operated glass-ring stirrer surrounded the bulb of a fractional degree thermometer immersed in the liquid. Time–temperature data were obtained after undercooling of the sample. Dried air was slowly passed through the apparatus to exclude moisture.

Analyses. Fluorine was determined by weighing as calcium fluoride and boron by titration with standard base in the presence of mannitol.[8]

Results and Discussion

Since distillation did not yield a satisfactory product, the melting points of some carefully prepared undistilled liquid samples were determined. In some preparations where no slight excess of either boron fluoride or water was present, the melting point was found to be quite sharp and significantly higher than previously reported values. Meerwein and Pannwitz[5] and Klinkenberg and Ketelaar[9] reported melting points of 4.5–5°.. Our carefully prepared undistilled samples melted at 5.9–6.1°. The liquid was clear, non-viscous and non-fuming and showed no attack on glass containers or change in melting point after standing a year at room temperature. Meerwein[4] reported d^{20}_4 1.623 for the distilled product; our undistilled material gave values of d^{20}_4 1.6315 and d^{25}_4 1.6252.

That the melting point of the undistilled boron fluoride dihydrate was a maximum was shown by separation of the product into 10 portions by fractional freezing. Fractions of identical melting point were obtained. In some preparations, containing an excess of either water or boron fluoride, the initial melting points were lower by several tenths of a degree. Fractional freezing of these products enabled a high yield of pure material to be obtained. Analysis for boron and fluorine gave results in good agreement with the calculated values. Careful weighing of the water and the observation that complete absorption of the gas took place enabled the composition to be checked synthetically. That the melting point was a maximum in the vicinity of composition, $BF_3 \cdot 2H_2O$, was demonstrated by the addition of small amounts of water and boron fluoride to the liquid. The presence of 0.2% of excess water lowered the melting point 0.1° and decreased its sharpness. Addition of excess boron fluoride had a similar effect.

Numerous distillations of the pure boron fluoride dihydrate were carried out in the pressure range 1–100 mm. At pressures below 10 mm. complete distillation takes place over a range of 1 to 2° but examination of separate fractions showed a gradual decrease in density. In a typical case 5 fractions from a distillation at 10 mm. gave densities varying from 1.6269 to 1.5934 at 25°. The first fractions in all distillations are noticeably more viscous than the starting material.

At pressures as high as 25 mm. the material distills over a sufficient range to permit separation into two constant-boiling portions. The lower-

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[4] Meerwein, *Ber.*, **66**, 411 (1933).

[5] Meerwein and Pannwitz, *J. prakt. Chem.*, **141**, 123 (1934).

[6] Booth, "Inorganic Syntheses," Vol. I, McGraw-Hill Book Co., New York, N. Y., 1939, p. 21.

[7] Dunoyer, "Vacuum Practice," 1st ed., D. Van Nostrand Co., New York, N. Y., 1926, p. 11.

[8] Pflaum and Wenzke, *Ind. Eng. Chem., Anal. Ed.*, **4**, 392 (1932).

[9] Klinkenberg and Ketelaar, *Rec. trav. chim.*, **54**, 959 (1935).

boiling, viscous fraction distills at 25 mm. at 85° and the higher-boiling at 93–95°. The 85° fraction constitutes 27% by weight of the starting material and has the following physical constants d^{20}_{4} 1.6788, n^{20}_{D} 1.3411. Analyses for boron and fluorine indicated a composition, $H_3BO_2F_2$. This fraction is undecomposed on subsequent distillation, even at atmospheric pressure, and has very nearly the same physical constants as the dihydroxyfluoboric acid reported by Sowa, Kroeger and Nieuwland.[10] Further confirmation of the composition of this product was obtained by its preparation from water, boron fluoride and boric acid by the reaction

$$2BF_3 + 3HOH + H_3BO_3 = 3H_3BO_2F_2$$

Boron fluoride is very readily absorbed by a suspension of boric acid in water, in the proportions called for by the above equation, to give a quantitative yield of $H_3BO_2F_2$. This 85° product undercools to an extremely viscous liquid, melts over a range, and becomes completely liquid at −2.2°.

The higher boiling fraction from the decomposition of boron fluoride dihydrate shows characteristics of a mixture of several compounds which cannot be separated by redistillation. It decomposes on distillation above 100 mm. pressure and has a melting point of 4–5°. Glass containers are slowly etched by this fraction. Analyses gave for B 9.7% and F 58.4%. The theoretical for $BF_3 \cdot 2H_2O$ is B 10.4% and F 54.9%.

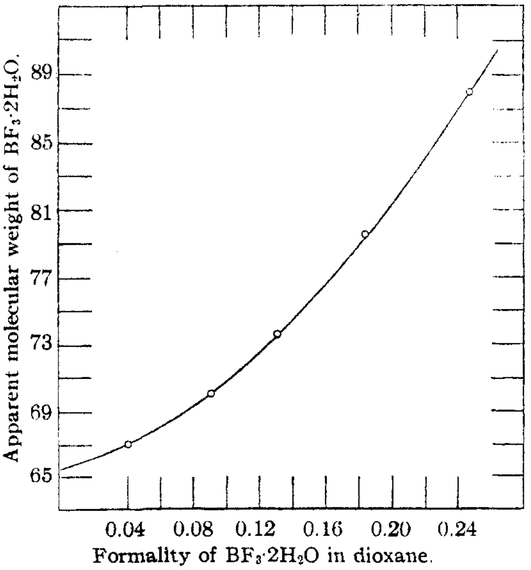

Fig. 1.—Apparent molecular weight of $BF_3 \cdot 2H_2O$ in dioxane solution from cryoscopic measurements.

The identification of the lower boiling fraction from the decomposition of boron fluoride dihydrate as dihydroxyfluoboric acid and the analysis of the higher boiling fraction enables an equation for the decomposition to be written

$$3(BF_3 \cdot 2H_2O) \rightarrow H_3BO_2F_2 + HF \cdot 2BF_3 \cdot 4H_2O$$

The weight per cent. of dihyroxyfluoboric acid obtainable from boron fluoride dihydrate on the basis of the above equation is 26.9. The observed weight per cent. in the distillation was 27. The exact molecular nature of the higher boiling fraction has not been determined.

A closed-system distillation under high vacuum was attempted but it was found that an irreversible increase in pressure resulted from heating boron fluoride dihydrate in glass. The non-condensable gas was pumped off and collected at atmospheric pressure by means of the Sprengel pump. The gas was identified as silicon tetrafluoride and is formed by the action of hydrogen fluoride on the glass container. Hydrogen fluoride is probably present as a constituent of the higher boiling fraction from the decomposition of boron fluoride dihydrate.

The sharp maximum melting point of boron fluoride dihydrate indicates that the substance is a definite compound at least in the solid state. Klinkenberg and Ketelaar[9] from X-ray spectra concluded that the compound had the structure of a hydronium salt of monohydroxyfluoboric acid. Its nature in the liquid state, as consisting of a single molecular species or as an equilibrium mixture, is uncertain from any previous work. In order to obtain some information on this point freezing point determinations on solutions of boron fluoride dihydrate in dioxane, with which it forms a soluble complex,[4,5] were made. The apparent molecular weight obtained from these data by extrapolation to infinite dilution was 66. The formula weight of $BF_3 \cdot 2H_2O$ is 103.8. A rapid increase in apparent molecular weight occurs on increasing concentration as indicated in Fig. 1. The extensive dissociation which occurs in dilute dioxane solution is an indication that in the liquid state boron fluoride may also be dissociated into an equilibrium mixture of hydroxyfluoboric acids.

The strongly acid character of boron fluoride dihydrate is well known but no salts of an acid of composition $BF_3 \cdot 2H_2O$ have been prepared. A white crystalline solid insoluble in dioxane is readily formed on addition of sodium to a dioxane solution of boron fluoride dihydrate but readily decompose on heating and is evidently not a stable salt of this acid. Further studies, now in progress, on the salts derived from boron fluoride dihydrate may enable the constituents of the equilibrium mixture, probably present in boron fluoride dihydrate, to be identified.

Summary

1. Pure boron fluoride dihydrate has been prepared and some of its physical constants determined.

2. Distillation has been shown to cause decomposition into dihydroxyfluoboric acid and other unidentified acids.

3. Cryoscopic evidence of the dissociation of boron fluoride dihydrate in dioxane solution has been obtained.

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[10] Sowa, Kroeger and Nieuwland, This Journal, **57**, 454 (1935).