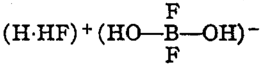
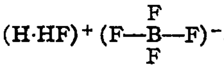
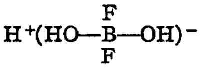
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

The Preparation of a New Hydroxyfluoboric Acid

BY F. J. SOWA, J. W. KROEGER AND J. A. NIEUWLAND

The existence of complex acids of boron and fluorine has been known for some time and their properties have been the basis of considerable study. Berzelius[1] prepared a complex acid of boron and fluorine to which he assigned the formula $H_2B_2O_4 \cdot 6HF$. By the action of boron fluoride on alcohol he also prepared the compound $HBO_2 \cdot 3HF$ (b. p. 92° at 30 mm.) which, it may be noticed, has just half the molecular formula of the first compound. Landolph[2] claimed to have isolated an acid $H_2B_2O_7 \cdot 3HF$ (b. p. 160°) by treating amylene with boron fluoride. By passing boron fluoride into water, Meerwein and collaborators[3,4] obtained a compound $BF_3 \cdot 2H_2O$ (b. p. 58.5–60° at 1.2 mm.; f. p. 4.6–5.0°). An acid having the same molecular formula as that of Meerwein has been reported by various early investigators[2,5] who report in most cases as a hydrofluoride of metaboric acid ($HBO_2 \cdot 3HF$). This may also be written  $(H\cdot HF)^+(HO\text{—}\overset{F}{\underset{F}{B}}\text{—}OH)^-$ by analogy to the compound[6]  $(H\cdot HF)^+(F\text{—}\overset{F}{\underset{F}{B}}\text{—}F)^-$. Travers and Malaprade[7] state that fluoboric acid decomposes in water solutions but the products which they isolated contained no oxygen.

In the preparation[8] of boron fluoride from calcium fluoride, boric oxide and sulfuric acid, it was noted that a liquid distilled from the generator and collected in the first trap. This liquid exhibited a constant boiling point even on the first distillation. It was found to correspond to the formula $H_3BO_2F_2$ or $HBO_2 \cdot H_2F_2$ and may be written structurally as  $H^+(HO\text{—}\overset{F}{\underset{F}{B}}\text{—}OH)^-$ by analogy to fluoboric acid $H^+BF_4^-$. Throughout this work the compound will be referred to as dihydroxyfluoboric acid. To the best of our knowledge, it was first purified and identified in this Laboratory.

The reactions taking place in the boron fluoride generator may be written

$$CaF_2 + H_2SO_4 \longrightarrow CaSO_4 + H_2F_2$$
$$4B_2O_3 + 9H_2F_2 \longrightarrow 6(HBO_2 \cdot H_2F_2) + 2BF_3$$

Due to the fact that sulfuric acid is used in excess rather than in the molar ratio the following reaction, to some extent, also takes place

$$6(HBO_2 \cdot H_2F_2) \longrightarrow 4BF_3 + B_2O_3 + 9H_2O$$

Dihydroxyfluoboric acid is identical with the compound formed by removing one molecule of HF from $BF_3 \cdot 2H_2O$. Due to their close relationship, it retains many of the properties of boron fluoride, in particular those of a catalytic nature. Since it is quite stable in the absence of moisture, and is easily handled and recovered, dihydroxyfluoboric acid is preferable as a catalytic agent. It may be prepared conveniently in the laboratory by either Methods (II) or (III) below.

Hydrolysis of dihydroxyfluoboric acid takes place in two stages. The first compound (m. p. 146°) formed still contains fluorine. Further treatment of this compound with a small amount of water results in the formation of metaboric acid (m. p. 173°). Previous preparations of metaboric acid consisted simply in heating a mixture of boric oxide and orthoboric acid. This mixture, however, loses water at 100° and does not have a definite melting point. Metaboric acid as prepared from dihydroxyfluoboric acid melts sharply at 173° and is apparently a definite compound.

The action of dihydroxyfluoboric acid as a catalytic agent is now being investigated for a number of different reactions, notably, the rearrangement of phenyl ethers, the condensation of alkenes and alkynes with acids, alcohols, phenols, benzene and hydrogen halides, and the esterification of organic acids. In esterification dihydroxyfluoboric acid gives better yields than boron fluoride, and in addition the catalyst can be recovered and used repeatedly. The water formed in the reaction evidently does not destroy the dihydroxyfluoboric acid, in this case.

Experimental Part

Preparation of Dihydroxyfluoboric Acid.—Dihydroxyfluoboric acid was prepared by each of the following methods

$$9CaF_2 + 4B_2O_3 + 9H_2SO_4 \longrightarrow 9CaSO_4 + 6(HBO_2 \cdot H_2F_2) + 2BF_3 \quad (I)$$
$$4B_2O_3 + 9H_2F_2 \longrightarrow 6(HBO_2 \cdot H_2F_2) + 2BF_3 \quad (II)$$

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(1) Berzelius, *Pogg. Ann.*, **58**, 503 (1843).
(2) Landolph, *Ber.*, **12**, 1583 (1879).
(3) Meerwein and Meier-Hüser, *ibid.*, **66**, 411 (1933).
(4) Meerwein and Pannwitz, *J. prakt. Chem.*, **141**, 123 (1934).
(5) Basarow, *Ber.*, **7**, 823 (1874).
(6) Hantzsch, *ibid.*, **63**, 1789 (1930).
(7) Travers and Malaprade, *Bull. soc. chim.*, **47**, 788 (1930).
(8) Bowlus and Nieuwland, THIS JOURNAL, **53**, 3835 (1931).

$$4H_3BO_3 + 2BF_3 \longrightarrow 2(HBO_2{\cdot}H_2F_2) + 4HBO_2 + H_2F_2 \quad \text{(III)}$$

$$HBO_2 + H_2F_2 \longrightarrow (HBO_2{\cdot}H_2F_2) \quad \text{(IV)}$$

$$4H_2O + 2BF_3 \longrightarrow 2(HBO_2{\cdot}H_2F_2) + H_2F_2 \quad \text{(V)}$$

Methods (I) and (II) are similar. Also, methods (III) and (V) are probably similar. The boric acid in (III) supplies the water for the reaction. In the case of Method (III) only a small amount of hydrogen fluoride was given off and only at the beginning of the experiment. A larger yield of dihydroxyfluoboric acid was obtained than could be expected from the equation as written. Apparently a secondary reaction (IV) takes place. Equations (III) and (IV) may now be combined

$$4H_3BO_3 + 2BF_3 \longrightarrow 3(HBO_2{\cdot}H_2F_2) + 3HBO_2 \quad \text{(VI)}$$

Method I.—The distillate from the boron fluoride generator[8] was collected by means of a trap and purified by distillation. The dissolved boron fluoride was evolved during the first part of the distillation. The remainder of the liquid distilled from 159–160°.

Method II.—Boric oxide (573 g.) was weighed into a copper vessel. Anhydrous hydrogen fluoride was passed in until an increase in weight (510.0 g.) was produced corresponding to slightly less than the theoretical requirement. The absorption was very rapid throughout and the vessel became quite warm. Boron fluoride was formed but remained in solution as long as the reaction vessel was kept cool. The liquid was decanted from the excess boric oxide and distilled. Practically all distilled from 159–160°. A 93% yield of dihydroxyfluoboric acid was obtained on the basis of the hydrogen fluoride absorbed.

Method III.—An excess of boron fluoride was passed into solid orthoboric acid contained in a Pyrex flask. The contents of the flask soon became warm and liquefied. The liquid was distilled and gave a quantitative yield of dihydroxyfluoboric acid. The residue was shown to contain only a slight trace of fluorine and was identified by analysis as metaboric acid (m. p. 173°). The yield was nearly quantitative: found, boron, 24.9, 23.1; calcd. (HBO_2), 24.6.

Method IV.—Anhydrous hydrogen fluoride was passed into a previously heated equimolecular mixture of orthoboric acid and boric oxide. Dihydroxyfluoboric acid was obtained on subsequent distillation.

Method V.—Boron fluoride was passed into water until the increase in weight corresponded to the ratio $1BF_3$ to $2H_2O$ and the solution was then distilled at atmospheric pressure. Hydrogen fluoride was given off and a small amount of dihydroxyfluoboric acid was isolated. The yield was only 3 to 5%.

This method is very unsatisfactory, but it is significant, namely, that with any solution or mixture containing boron fluoride, where water is present as an impurity or formed during a reaction, there is a possibility for the formation of dihydroxyfluoboric acid.

Properties of Dihydroxyfluoboric Acid.—Dihydroxyfluoboric acid does not etch glass and so can be kept in glass bottles. It is quite stable in an atmosphere free from moisture. The pure acid is a colorless, sirupy liquid which fumes slightly when brought into contact with moist air. Dihydroxyfluoboric acid distils at 159.1° (745 mm.), 114° (141 mm.), 101.5° (68 mm.), 89.5° (38 mm.) and 69° (4 mm.). The surface tension is 58.294 dynes/sq. cm. (25°); n^{30}_{D} 1.3414; sp. gr. 1.6569 (25°) and 1.6539 (30°). It does not crystallize at as low as −20° but becomes exceedingly viscous. The conductivity of the pure acid is of the same order as that of concentrated sulfuric acid. From vapor density measurements, it was found that the compound is dissociated in the vapor phase. It is soluble in ether–boron fluoride, acetic acid–boron fluoride and alcohol-boron fluoride; it is insoluble in carbon tetrachloride, carbon bisulfide, benzene and similar solvents.

Treatment of dihydroxyfluoboric acid with water, ether, methyl or ethyl alcohol or acetic acid results in the formation of an amorphous white precipitate (m. p. 146°) which still contains fluorine and which, on further treatment with any of these reagents or simply by heating at 80° for twenty-four hours, forms metaboric acid (m. p. 173°). During the distillation of dihydroxyfluoboric acid a small amount of white solid matter usually collects in the condenser. This is identical with the first compound mentioned above. Using the method of Meerwein and Pannwitz $BF_3{\cdot}2H_2O$ was prepared and found to undergo a similar decomposition. The compound first formed (m. p. 146°) decomposed to metaboric acid.[9]

Iron, sodium, calcium, magnesium and zinc displace hydrogen from dihydroxyfluoboric acid, in some cases forming a gas having the odor of diborane. The acid reacts with cupric oxide but not appreciably with cuprous oxide; it forms a yellow compound with mercuric oxide and decomposes alkali hydroxides and carbonates, and potassium permanganate. It reacts with sodium chloride to form hydrogen chloride and water together with an unidentified sodium salt. It absorbs boron fluoride in equimolecular proportions and the boron fluoride is evolved by merely heating the solution. By warming equal volumes of the pure acid and concentrated sulfuric acid, the dihydroxyfluoboric acid is decomposed to form boron fluoride according to the reaction

$$6(HBO_2{\cdot}H_2F_2) \longrightarrow 4BF_3 + B_2O_3 + 9H_2O$$

Dihydroxyfluoboric acid forms definite solid compounds with dioxane, cineol, acetic anhydride and acetyl chloride, the product from the last two being identical.

Analytical.—The analyses for boron and fluorine in dihydroxyfluoboric acid were conducted according to the method of Pflaum and Wenzke.[10]

Anal. Calcd.: F, 45.33; B, 12.80; mol. wt., 83.8; one-half mol. wt., 41.9. Found: F, 44.84, 44.98, 45.01; B, 13.33, 13.31; mol. wt., 41.3, 41.6 (vapor density method).

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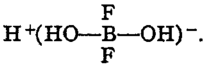
[9] Dihydroxyfluoboric acid and $BF_3{\cdot}2H_2O$ were found to have identical boiling points at low pressures 73–74° (6 mm.). Dihydroxyfluoboric acid can be distilled at atmospheric pressure but $BF_3{\cdot}2H_2O$ decomposes. The boiling point of dihydroxyfluoboric acid is really a decomposition point since its vapor is dissociated. It may be that $BF_3{\cdot}2H_2O$ and dihydroxyfluoboric acid have identical products of decomposition (HF and $FB(OH)_2$) and for this reason have the same decomposition temperatures at low pressures. At high pressures the products of decomposition of $BF_3{\cdot}2H_2O$ do not recombine to form the original compound but give off hydrogen fluoride and form dihydroxyfluoboric acid.

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

Proof of Structure of Dihydroxyfluoboric Acid.—The analyses and molecular weight determinations indicated a compound having a molecular formula H_3BF_2O. The presence of one strongly acidic hydrogen atom was indicated by the fact that dihydroxyfluoboric acid reacted in molar proportions with sodium chloride forming hydrogen chloride. The resulting sodium salt lost water, which indicates the attachment of two hydroxyls to the same atom. The presence of the two hydroxyl groups was shown by the fact that one mole of dihydroxyfluoboric acid reacted with two moles of acetyl chloride to form hydrogen chloride, acetic acid–boron fluoride ($CH_3COOH_2 \cdot BF_3$), acetic acid and a solid compound identical with that obtained from acetic anhydride. This derivative crystallized from hot acetyl chloride in the form of long needles having a melting point of 202–203°, and contained boron and fluorine in the ratio of approximately one to one. It formed a white solid compound on treatment with mercuric oxide, which was insoluble in acetyl chloride. Further work is being done at present in order to establish the structure of this acetoxy derivative. The acid characteristics of dihydroxyfluoboric acid are further indicated by its reactivity toward alkali hydroxides and carbonates and by its catalytic effect on esterification reactions.

On the basis of this information we may write the following tentative structure for dihydroxyfluoboric acid:



$$H^+(HO{-}\overset{F}{\underset{F}{B}}{-}OH)^-.$$

Summary

1. A new liquid, anhydrous, inorganic acid of the hydroxyfluoboric type has been prepared.
2. Several methods of preparation have been given.
3. A structure has been assigned it tentatively.
4. Some of its properties and acidic reactions have been studied.
5. Some of its possibilities as a catalytic agent have been mentioned.
6. Pure metaboric acid has been prepared and its melting point has been determined.

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Photochemical Studies. XXI. The Absorption Spectrum of Germane

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The decomposition of germane sensitized by mercury vapor has been investigated.[1] At the same time it was observed that germane could be decomposed photochemically in the absence of mercury vapor by the action of radiation from a hydrogen discharge tube which had traversed thin layers of quartz. The final products in both cases were metallic germanium and hydrogen. No absorption due to germane was found with the aid of a quartz spectrograph (2100–7000 Å.).

In the present investigation the absorption spectrum of germane has been photographed in the fluorite region and estimates made of the absorption coefficients at several wave lengths. An attempt has been made to determine the nature of the primary step in the direct photochemical decomposition of germane.

I. Experimental

The preparation and purification of the germane have been described.[1,2,3] Due to the fact that metallic germanium is deposited during photochemical decomposition of the germane, it was not deemed advisable to use this substance in the vacuum grating spectrograph. The present study was made, therefore, with a small fluorite spectrograph of the type described by Cario and Schmidt-Ott.[4] It was modified slightly so that four exposures could be taken on one plate without breaking the vacuum. The spectrograph was evacuated by a butyl phthalate diffusion pump.

A water-cooled hydrogen discharge tube of the type described by Bay and Steiner[5] was used as a light source. It was operated on two kilowatts without a condenser in the secondary circuit.

The absorption cell was of Pyrex, 6.3 mm. in length, one end of which was waxed directly to the window of the discharge tube, while the other was similarly fastened to the window of the spectrograph.

Eastman Ultraviolet Sensitive plates were used.

Qualitative estimates of absorption coefficients were made by the method of varying times of exposure.[6] The results are admittedly very inaccurate, but serve to give the order of magnitude.

II. Results

With fluorite windows on the cell the photochemical decomposition proceeded very rapidly and the windows of the absorption cell became opaque due to the deposited germanium. With

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[1] Romeyn and Noyes, This Journal, **54**, 4143 (1932).

[2] Kraus and Carney, *ibid.*, **56**, 765 (1934).

[3] Teal, Ph.D. Thesis, Brown University, 1930. The germane used in these experiments was prepared by Dr. Teal.

[4] Cario and Schmidt-Ott, *Z. Physik*, **69**, 719 (1931).

[5] Bay and Steiner, *ibid.*, **45**, 337 (1927).

[6] Weigert, "Optische Methoden der Chemie," Akademische Verlagsgesellschaft, Leipzig, 1927, p. 223.