fractional crystallization of the free fatty acids of *H. Wightiana*, *H. anthelmintica* or *T. Kurzii* oils always yielded mixtures which melted at 48–50°C.[1] They concluded that they were dealing with a molecular mixture of chaulmoogric acid and its homolog, hydnocarpic acid. By making up mixtures of these two pure acids and plotting the melting point curve, it was found that the lowest melting mixture was not at the point of a molecular mixture. Mixtures of the two acids do show, however, a very sharp drop in melting point and a loss of the characteristic crystalline formation of the pure acids (Fig. 2).

Optical Rotation

Because of the very high specific optical rotations of hydnocarpic and chaulmoogric acids (69.3 and 60.3°, respectively), the determination of this value is a very convenient means of ascertaining the purity of the acid. Especially is this so when one is able to employ, as we have done, an electric sodium lamp in conjunction with a precision polarimeter. Two different observers have been able to check readings with each other within ±0.02°.

The specific optical rotation of chaulmoogric acid often has been reported too high because there has been mixed with it a small amount of the more optically active hydnocarpic acid. Thus Stanley and Adams[3] report +61.9°, Power and Barrowcliff[1], +62.1° and Hinegardner and Johnson,[4] +62.2°. Goulding and Akers[5] report +60.0° while we obtain +60.3°.

In the case of hydnocarpic acid most of the optical rotation values given in the literature are too low due to the presence of palmitic or even chaulmoogric acid. We, however, closely check the value given by Stanley and Adams,[6] +69.4°, although their value for ethyl hydnocarpate, +70.5°, evidently is in error.

CALCULATIONS FOR SPECIFIC OPTICAL ROTATION

Compound	Source, oil of	Grams	$CHCl_3$, cc.	Ang. rotn., 100-mm. tube	$[\alpha]^{15}_D$
Chaulmoogric acid	*H. Wightiana*	2.5526	25	+6.16°	+60.3°
Chaulmoogric acid	*O. echinata*	3.2175	25	+7.77°	+60.3°
Ethyl chaulmoograte	*O. echinata*	2.6479	25	+5.87°	+55.42°
Hydnocarpic acid	*H. Wightiana*	4.9422	50	+6.86°	+69.3°
Ethyl hydnocarpate	*H. Wightiana*	1.9978	25	+4.95°	+61.94°

Summary

The published data on the physical constants of hydnocarpic and chaulmoogric acids and ethyl esters are incomplete and inaccurate. Methods of preparation of the pure acids and ethyl esters are described and their physical constants have been determined. The melting point curves for mixtures of hydnocarpic and palmitic and of hydnocarpic and chaulmoogric acids have been determined.

(3) W. M. Stanley and R. J. Adams, THIS JOURNAL, **48**, 2395 (1926).

(4) W. S. Hinegardner and T. B. Johnson, *ibid.*, **51**, 1503 (1929).

(5) E. Goulding and N. C. Akers, *Proc. Chem. Soc.* (London), **29**, 197 (1913).

(6) W. M. Stanley and Roger Adams, THIS JOURNAL, **51**, 1515 (1929).

RIO DE JANEIRO, BRAZIL RECEIVED FEBRUARY 9, 1937

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

Some Reactions of Dihydroxyfluoboric Acid

BY J. W. KROEGER, F. J. SOWA AND J. A. NIEUWLAND[1]

A previous paper[2] from this Laboratory described the preparation and some of the properties of dihydroxyfluoboric acid and advanced a tentative structure for this compound. The present work was undertaken in order to throw some light on the structure of this acid and to present certain peculiar reactions which it undergoes.

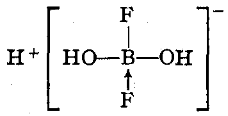
The literature on the various acids of boron and fluorine has been reviewed by Meerwein and Pannwitz[3] and by the authors.[2] Meerwein describes a compound which he calls boron fluoride-dihydrate which is striking in its similarity to dihydroxyfluoboric acid. They have similar boiling and melting points, their indices of refraction and densities agree rather closely and the melting points of their dioxane derivatives are practically the same.

Dihydroxyfluoboric acid may be written in any of three ways

(1) The major portion of this work was completed before the death of Dr. Nieuwland in June, 1936.

(2) Sowa, Kroeger and Nieuwland, THIS JOURNAL, **57**, 454 (1935).

(3) Meerwein and Pannwitz, *J. prakt. Chem.*, **141**, 123 (1934).



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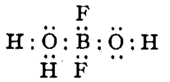

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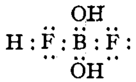

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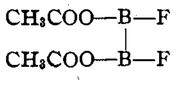
The first structure is the formal representation for this type of acid. The major part of the acid probably exists in the form of the second structure with the hydrogen ion coördinating with one of the hydroxyl groups. This is supported by the fact that dihydroxyfluoboric acid will combine with only one mole of boron trifluoride, probably through coördination with the second hydroxyl group. However, the possibility of the hydrogen ion coördinating with one of the fluorine atoms must also be admitted.

One hydrogen atom, as is represented in formula I, is available for salt formation. The others are alcoholic in their reactivity, or more properly, they resemble the hydrogen atoms in orthoboric acid. Sodium chloride reacts mole for mole with dihydroxyfluoboric acid with evolution of hydrogen chloride. The nickel salt crystallizes with three molecules of acid of crystallization as $Ni(H_2BO_2F_2)_2 \cdot 3H_3BO_2F_2$, but the unsolvated salt cannot be well characterized.

Dihydroxyfluoboric acid, in spite of the fact that it contains only two atoms of fluorine, forms boron trifluoride when it reacts. This is shown by the reaction with acetyl chloride and acetic anhydride, with oxygen compounds and with benzenediazonium chloride.

The hydrogen atoms of the two hydroxyl groups may be acetylated either with acetic anhydride or with acetyl chloride but, as yet, a stoichiometric equation cannot be written for the reaction. The products in the latter case are hydrogen chloride, acetic acid, acetic acid-boron fluoride $[(CH_3COOH)_2 \cdot BF_3]$ and an acetoxy boron fluoride having the formula $(CH_3COOBF)_2$. This compound must be written in either of two ways



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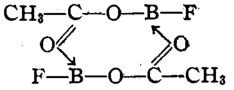

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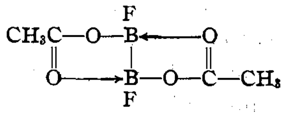
Acetoxyboron fluoride is a crystalline compound melting at 206–207° which sublimes with some decomposition *in vacuo*, is decomposed by water and most organic compounds containing oxygen (with the exception of acetyl chloride and acetic anhydride) and which has no reducing properties. Formula II is extremely unlikely since a seven electron shell about a boron atom is highly improbable. Formula I is more probable from a structural point of view. However, it is difficult to see how a boron-to-boron linkage could be formed from dihydroxyfluoboric acid. A third structure, a combination of the two previous, is somewhat more likely



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if the formation of a boron-to-boron link is admitted to be possible.

Experimental and Discussion

Preparation of Dihydroxyfluoboric Acid.—The preparation of this acid has been somewhat modified for the sake of speed and convenience.

Seven hundred and seventy grams of liquid hydrogen fluoride were run into a 1000-ml. copper beaker cooled in an ice-bath. After the hydrogen fluoride had cooled to approximately the temperature of the bath, 500 g. of boric oxide was added slowly. A rather violent reaction took place immediately and was accompanied by evolution of boron trifluoride. When about half the boric oxide had been added it was found necessary to run in 300 g. more hydrogen fluoride because of loss from evaporation. The reaction time for these amounts of reagents was two hours.

The copper beaker and contents were then heated to 80° for a half hour to drive off dissolved gases, after which the reaction mixture was poured into a Claisen flask. The liquid at this point weighed 1014 g. and since the theoretically possible quantity of acid is 903 g. it was concluded that the mixture still contained a large amount of dissolved gases. After two distillations in vacuum, 890 g. of pure dihydroxyfluoboric acid was obtained, b. p. 159–160° (745 mm.), 93–95° (25 mm.), 84–86° (16 mm.); m. p. 4.0–4.5°; n^{25}_{D} 1.3323; d^{25}_{4} 1.6560.

The molecular refraction of this acid could be calculated using the following linkage values: HO—B—OH[4] 7.05, H—F[5] 1.9 and B—F[6] 2.0. These values show the calculated molecular refraction of dihydroxyfluoboric acid to be 10.95. A carefully fractionated sample had the constants n^{30}_{D} 1.3414, d^{30}_{4} 1.6539. From these constants the observed molecular refraction is 10.68.

Conductivity of Dihydroxyfluoboric Acid.—The conductivity of the acid was determined with the usual Kohl-

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(4) Otto, unpublished work, University of Notre Dame. This value was calculated from the molecular refraction of orthoboric acid in dioxane (10.57).

(5) Smyth, "Dielectric Constant and Molecular Structure," A. C. S. Monograph, 1931, p. 149.

(6) Klemm, *Z. anorg. allgem. Chem.*, **213**, 115 (1933). Klemm found the molecular refraction of boron trifluoride to be 6.0.

rausch assembly at 25°. The resistance was 2867 ohms, cell constant 56.052, specific conductivity 0.0195 mhos, molal conductivity 0.988 mhos.

Dioxane Derivative.—Five grams of dihydroxyfluoboric acid was treated with 5.9 g. of dioxane in 15 ml. of petroleum ether. The solid which separated was recrystallized from a mixture of dioxane and petroleum ether. The large, brittle, apparently non-hygroscopic crystals were powdered and found to melt at 139.5–140.5°. Calcd. for $C_4H_8O_2 \cdot H_3BO_2F_2$ (%): boron, 6.28; fluorine, 22.1. Found: boron, 6.27; fluorine, 22.1.

Acetylation of Dihydroxyfluoboric Acid.—Approximately one-half mole (46.1 g.) of dihydroxyfluoboric acid was weighed into a flask cooled in an ice-bath. One and one-half moles of acetyl chloride (120 g.) was dropped in over a period of two hours. Hydrogen chloride came off immediately and was passed through a trap cooled in ice into a solution of sodium hydroxide. The evolution of hydrogen chloride practically ceased when about 85 ml. of acetyl chloride had been added; however, the remainder was run in in order to decrease the solubility of acetoxyboron fluoride in the reaction mixture. The flask was then warmed to about 40° and swept out with dry air to remove the remaining hydrogen chloride. It was found that the weight of the absorber had increased 42.8 g. Back-titration of the remaining sodium hydroxide indicated that 40.2 g. of hydrogen chloride had been absorbed. The discrepancy between this value, which is very near the calculated figure (40.1 g.), and the actual weight was probably due to some entrainment of acetyl chloride.

The reaction mixture was let stand overnight to permit crystallization of the acetoxyboron fluoride. The liquid was then decanted and the crystals were washed with a small amount of acetyl chloride. When crystallization did not take place the liquid reaction mixture was distilled directly and the residue was recrystallized from acetyl chloride from which it separated in long needles. The following are the results obtained from the experiment described above.

TABLE I

Product	B. p., °C.	Yield, g.	n^{25}_D
HCl	.....	40.2	....
CH_3COOH	116–117	11.9	1.3730
$(CH_3COOH)_2 \cdot BF_3$	64–66 (15 mm.)	51.5	1.3735
$(CH_3COOBF)_2$	M. p. 206–207°	19.3	....

Acetoxyboron fluoride was analyzed for boron and fluorine according to the procedure of Pflaum and Wenzke,[7] modified by decomposing the sample with sodium in liquid ammonia as described by Vaughn and Nieuwland.[8]

The acetyl determination was carried out in the following manner. Accurately weighed samples of acetoxyboron fluoride, usually about 1.5 g., were dissolved in 10 to 15 g. of absolute ethyl alcohol and refluxed for two hours. The mixture was then distilled until the temperature reached 85°, the distillate being collected in 250 ml. of 0.1 N sodium hydroxide. To the residue was added 15 g. of absolute alcohol and, after refluxing and distilling as before, the residue was again treated with absolute alcohol and the procedure repeated. All parts of the apparatus except the actual reaction flask were then rinsed with absolute alcohol which was added to the flask containing the distillate and 0.1 N sodium hydroxide. This was allowed to stand overnight and was then titrated with 0.1 N hydrochloric acid using phenolphthalein as an indicator. From this, the amount of ethyl acetate in the distillate could be found and consequently the percentage of acetyl in the original compound. It was found that the distillate contained only traces of boron and no fluorine. Two treatments with absolute alcohol, as described above, were sufficient to remove all the acetoxy but the third was always included to ensure certainty in the results. Eight to twelve hours was found to be ample for the saponification of the ethyl acetate. The results obtained were, calcd.: acetoxy, 66.46; boron, 12.16; fluorine, 21.39; total 100.0. Found: acetoxy, 65.4; boron, 12.16; fluorine, 21.09; total 98.7. A qualitative test for chlorine was found to be negative.

The molecular weight of acetoxyboron fluoride was determined ebullioscopically in acetyl chloride. Mathews and Fehlandt[9] give a value for the heat of vaporization of acetyl chloride at 50.4° equal to 87.14 ± 0.09 cal./g. The ebullioscopic constant calculated from this value was found to be 2.38 degrees per mole per kilogram. This constant was checked experimentally using pure naphthalene, which gave a value of 2.21. A series of ten determinations of the molecular weight of acetoxyboron fluoride gave an average value of 175.5 ± 3.1. This value is approximately twice the formula weight of 88.8 so the formula of the compound must be $(CH_3COOBF)_2$.

Although acetoxyboron fluoride is rather insoluble in acetyl chloride, this solvent appears to be the only one in which there is no possibility of decomposition. It was thought that some light might be thrown upon the structure of this compound by a determination of the molecular refraction. The constants given below were all determined at 25°. Those for the pure solvent, acetyl chloride, were: d_4 1.0958, n_D 1.38613, MR_D calcd. 16.314, MR_D obs. 16.827. The values for the solution were d_4 1.1009, n_D 1.38646, c_2 0.0072116 moles/mole. These data give a value for the molecular refraction of 29.029. The calculated value, omitting the third valency of the boron atoms, is 30.268. This omission causes the calculated value to be low by at least one or two units; however, considering the extreme dilution of the solution and the lack of knowledge concerning the disposition of the third boron linkages, these values are in surprisingly good agreement.

Acetoxyboron fluoride is insoluble in most organic solvents and is decomposed by water and those containing oxygen. It may be crystallized from trimethyl borate if done quickly but on standing in contact with the solvent for more than a day it is decomposed.

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

[8] Vaughn and Nieuwland, *ibid.*, **3**, 274 (1931).

[9] Mathews and Fehlandt, THIS JOURNAL, **53**, 3212 (1931).

Referring to Table I it may be seen that, on the basis of one mole of dihydroxyfluoboric acid reacting, there are found in the products 0.984 atom of boron, 2.08 atoms of fluorine, 1.93 atoms of non-carbonyl oxygen but 3.594 atoms of hydrogen. The empirical formula for dihydroxyfluoboric acid is $H_3BO_2F_2$ and since the above value for hydrogen is definitely beyond the experimental error of the determination it is difficult to explain this discrepancy. Actual determinations of hydrogen by combustion methods gave a value of 3.37% as compared to the calculated value of 3.61%. In addition, when dihydroxyfluoboric acid is treated with sodium chloride exactly one mole of hydrogen chloride is given off.

One-third mole of dihydroxyfluoboric acid (28 g.) was dissolved in 200 g. of redistilled ether-boron fluoride b. p. 121–122° and 40 g. (excess) of powdered C. P. sodium chloride was added. The mixture was refluxed for three days and the hydrogen chloride which came off was dissolved in sodium hydroxide solution. Back-titration showed that 11.1 g. of hydrogen chloride had been absorbed. The calculated value, assuming only one hydrogen in dihydroxyfluoboric acid to be replaced, is 12.2 g. The reaction was very slow and probably did not go to completion.

Nickel Salts.—Since the nickel salt of dihydroxyfluoboric acid is quite readily prepared it was decided to utilize this as an additional method for characterizing the acid. This salt may be prepared without difficulty by dissolving nickelous carbonate or chloride in the acid but the oxides and hydroxide apparently do not react.

Slightly less than the calculated quantity of nickelous carbonate was dissolved in dihydroxyfluoboric acid by warming. The product, which solidified on cooling, was recrystallized from a small amount of pure acid. The resulting dark-green crystals were filtered with suction in a closed Gooch crucible and were quickly pressed dry on filter paper, then were analyzed for nickel using dimethylglyoxime. Calcd. for $Ni(H_2BO_2F_2)_2 \cdot 3H_3BO_2F_2$: Ni, 12.3. Found: Ni, 11.9, 12.1. This salt melted at 120°.

The salt was heated carefully and intermittently at 155–160° and 12 mm. pressure for a total period of twelve hours. Samples were removed at intervals of two to three hours and analyzed and in this way a material was obtained which corresponded to nickel dihydroxyfluoborate. Calcd. for $Ni(H_2BO_2F_2)_2$: Ni, 26.1. Found: Ni, 26.2, 26.2. This material, light green in color, is readily converted by heating for two to three hours at 200° and 12 mm. pressure to a creamy, fluffy powder. Calcd. for $Ni(HBO_2F)_2$, 31.8% Ni and for $Ni(BF_2O)_2$, 31.1% Ni; found, 31.0% Ni. The first salt might be formed by loss of hydrogen fluoride from the original material and the second by loss of water. The latter possibility was found to be the case since a small amount of water actually was collected during the second period of heating, that at 200°.

The cream colored salt was ignited in air at 900° for ten hours. The resulting greenish-black powder contained 60.1% Ni. After an additional ten hours of heating the percentage of nickel had risen to 61.7%. This material contained boron but no fluorine and was apparently a mixture of nickelous oxide and metaborate. Beginning with the original dark green crystalline salt, the solubility in water of the various compounds became smaller as heating progressed. The cream colored salt was only slightly soluble in water but soluble in dilute acids. The final oxide–metaborate mixture was insoluble in water and acids and in order to analyze for nickel the samples had first to be fused with sodium pyrosulfate. The remaining compounds were quite soluble in water.

Formation of Orthoboric Acid.—Dihydroxyfluoboric acid is decomposed by low-molecular weight acids, alcohols, esters, ketones, aldehydes and ethers, with the exception of dioxane, to form orthoboric acid and boron fluoride. This decomposition is apparently regulated by the ease of formation of the boron fluoride complex of the second reactant. Thus trichloroacetic acid, the boron fluoride complex of which is stable only at low temperatures, will not react with dihydroxyfluoboric acid even when melted, whereas acetic acid, which forms a stable addition compound boiling at 141–142°, reacts almost immediately.

The reaction always involves one mole of dihydroxyfluoboric acid and two moles of the second reactant. While the actual decomposition may be represented by the following scheme

$$3H_3BO_2F_2 \longrightarrow 2BF_3 + H_3BO_3 + 3H_2O$$

where the boron fluoride then forms a complex with the second reactant, it is difficult to understand why the additional amount of the oxygen compound is necessary. That is, three moles of the acid actually require six moles of the second reactant.[10] Two moles of an ether are required to combine with the boron fluoride liberated and either two or four moles of an acid or an alcohol ($ROH \cdot BF_3$ and $RCOOH \cdot BF_3$ or the more stable $(ROH)_2 \cdot BF_3$ and $(RCOOH)_2 \cdot BF_3$). In either case the amount is less than the six moles actually required. The boron fluoride and the orthoboric acid cannot be estimated accurately since the water formed in the reaction causes a secondary decomposition.

The boric acid from these decompositions, when filtered and pressed dry on filter paper,

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(10) This was determined by preparing tubes containing identical amounts of dihydroxyfluoboric acid and varying amounts of the reactant, centrifuging and weighing the orthoboric acid formed. The boron fluoride was also estimated where the second reactant formed a complex, stable to distillation, as in the case of ether, acetic acid and methyl and ethyl acetates.

contained from 6 to 10% fluorine, and 16.7 to 17.0% boron (calcd. for H_3BO_3, 17.5% B). The melting point was always about 148–149° and since pure boric acid melts at 175–176° it was thought that there must be some other compound present. When thoroughly washed with the secondary reactant the material contained no fluorine, the melting point rose to 175–176° and the percentage of boron rose to the calculated value, 17.5%. The same thing could be accomplished by drying in a vacuum over potassium hydroxide for two weeks. After drying for twelve hours at 110° the material contained no fluorine and was found to be metaboric acid, m. p. 175–176°, 24.6% B, calcd., 24.6%.[11]

Samples of pure orthoboric acid were moistened with ether–boron fluoride, acetic acid–boron fluoride and methyl acetate-boron fluoride and after filtering and pressing dry on filter paper, were found to have melting points between 149 and 151° and contained considerable amounts of fluorine. Apparently this was the explanation for the low melting points.

Orthoboric acid is also formed by the action of water on dihydroxyfluoboric acid, m. p. 175°, calcd. % B 17.5; found, 17.4.

Preparation of Fluorobenzene.[12]—The best results were obtained using a ratio of two moles of dihydroxyfluoboric acid to one of the diazonium salt. One-quarter mole of benzenediazonium chloride was prepared to which was added one-half mole (42 g.) of dihydroxyfluoboric acid while cooling to below 10°. The mixture was stirred for forty-five minutes, then filtered and the light-green precipitate was washed with small amounts of alcohol and ether: yield of salt, 43 g.; decomposition point, 84°. This salt was decomposed by warming and formed 11.8 g. of fluorobenzene, b. p. 84–85°. If this salt were $C_6H_5N_2BF_2(OH)_2$ the yield of fluorobenzene was 25%, whereas if the compound were $C_6H_5N_2BF_4$ the yield was 50%.

The purest salt was obtained by using a ratio of one mole of dihydroxyfluoboric acid to one of the diazonium compound. The yield was extremely poor but the salt decomposed at 85°. One-half gram of this material, accurately weighed, was decomposed by heating and the evolved gas was analyzed. The volumes were corrected for pressure, temperature and the vapor tension of water. A total of 115 ml. of gas was collected over mercury. After washing with water 56 ml. of nitrogen remained. Calculated: total, 116.8 ml.; BF_3, 58.4 ml.; N_2, 58.4 ml. These results indicate that the salt was benzenediazonium fluoborate $C_6H_5N_2BF_4$ and that it was about 95% pure.

Acknowledgment.—The authors are indebted to Dr. R. R. Vogt for valuable advice and criticism and to Dr. M. M. Otto, Messrs. V. P. Osweiler, C. R. Montgomery and F. J. Froning for assistance in various parts of this work.

Summary

1. Dihydroxyfluoboric acid has been shown to contain one strongly acidic and two nonacidic hydrogen atoms.

2. Several reactions of dihydroxyfluoboric acid have been discussed and their products identified.

3. Acetoxyboron fluoride has been prepared by acetylation of dihydroxyfluoboric acid and a proposed structure has been advanced.

NOTRE DAME, INDIANA RECEIVED MARCH 3, 1937

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[11] It was thought that the presence of another compound might appear in a determination of molecular weight. Trimethyl borate was chosen as a solvent. The melting point was found to be −29.4 ± 0.1° and the cryoscopic constant, determined experimentally using naphthalene, was 4.68 ± 0.1° per mole per kilogram. However, it was found that the boric acids dissociated in this solvent. Thus, metaboric acid had an apparent molecular weight of 29.5.

[12] "Organic Syntheses," **13**, 46 (1933).