Long and Dollimore :

363. The Chemistry of Boron. Part I. The Reactions and Structure of Dihydroxydifluoroboric Acid.

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The behaviour of dihydroxydifluoroboric acid, $H_3BO_2F_2$, towards halogenating agents—phosphorus trichloride, phosphorus pentachloride, phosphorus pentabromide, phosphorus tri-iodide, and thionyl chloride and towards phosphoric oxide has been studied. No reaction was observed with phosphorus trichloride. Otherwise reactions occurred which were characterised by the formation of boron trifluoride or boron phosphate or both.

No single reaction formula can be drawn up to explain the chemical behaviour of dihydroxydifluoroboric acid, and all known facts concerning this compound are best explained on the assumption that the anhydrous acid consists of an equilibrium mixture of associated molecular species in which hydrogen bonding plays an important part. The vapour probably consists of H_2O and BF_2 ·OH molecules, and it is considered improbable that the free $H_3BO_2F_2$ molecule is capable of independent existence.

ALTHOUGH dihydroxydifluoroboric acid, $H_3BO_2F_2$, has been known for a number of years, and some of its properties, particularly its catalytic behaviour, have been studied (Sowa, Kroeger, and Nieuwland, J. Amer. Chem. Soc., 1935, 57, 454; Kroeger, Sowa, and Nieuwland, *ibid.*, 1937, 59, 965; Doris, Sowa, and Nieuwland, *ibid.*, 1938, 60, 656; McGrath, Stack, and McCusker, *ibid.*, 1944, 66, 1263), much that is fundamental regarding its general chemical nature remains unknown. Accordingly its behaviour with halogenating agents has been examined, namely, with phosphorus trichloride, phosphorus pentachloride, phosphorus pentabromide, phosphorus tri-iodide and thionyl chloride, as well as the behaviour with phosphoric oxide. The results throw some light on the structure of the anhydrous acid. The preparation of dihydroxydifluoroboric acid was accomplished by two of the six methods previously reported (Sowa *et al.*, *loc. cit.*; McGrath *et al.*, *loc. cit.*).

Surprisingly, phosphorus trichloride was found not to react, even at its boiling point, but all the other substances mentioned reacted to different extents, yielding a variety of products. All the volatile products from these reactions were examined and identified by means of highvacuum technique.

Phosphorus pentachloride reacts with dihydroxydifluoroboric acid in equimolecular ratio with a copious evolution of hydrogen chloride, much of which is evolved in the cold and the remainder only on heating. Boron trifluoride is also liberated, the molecular ratio HCl: BF_3 being approximately 4:1. For every three molecules of dihydroxydifluoroboric acid destroyed two of phosphorus oxychloride were formed and one molecule of boron phosphate, which remained behind as an involatile and insoluble residue. The over-all equation

$$3H_3BF_2O_2 + 3PCl_3 \longrightarrow BPO_4 + 2POCl_3 + 2BF_3 + 9HCl_3$$

accords with the observed facts satisfactorily.

Dihydroxydifluoroboric acid reacts similarly with phosphorus pentabromide, except that no gas is evolved in the cold. On heating, hydrogen bromide and boron trifluoride are evolved, and, in addition to phosphorus oxybromide, boron phosphate is formed as before. An equation similar to that above is therefore postulated.

The reaction between dihydroxydifluoroboric acid and phosphorus tri-iodide is rather different. None occurs in the cold, but on moderately strong heating a reaction sets in which requires two molecules of phosphorus tri-iodide for every three of dihydroxydifluoroboric acid consumed. Hydrogen iodide, boron fluoride, and apparently hydrogen fluoride are liberated, although the latter was not identified as such and was inferred to be among the original products from the heavy vapour-phase attack on the walls of the glass apparatus and from the presence of silicon tetrafluoride. The main reaction is probably

$$3H_3BO_2F_2 + 2PI_3 \longrightarrow [B_2O_3, P_2O_3] + 6HI + BF_3 + 3HF$$

but there are side-reactions, as a small amount of iodine is liberated and a trace of a non-identifiable boron-containing liquid (b. p. \sim 76°) not attacked by water was obtained. The

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postulated residue, B_2O_3 , P_2O_3 ("boron phosphite," by analogy with boron phosphate, B_2O_3 , P_2O_5), could not be identified as such since, in common with many tervalent phosphorus compounds, it partly decomposes on strong heating with the liberation of finely divided elementary phosphorus, possibly according to the scheme $5B_2O_3$, $P_2O_3 \longrightarrow 6BPO_4 + 2B_2O_3 + P_4$. The pale orange residue, which was halogen-free, smelled of phosphorus, ignited on gentle heating in the air, and liberated phosphine with aqueous sodium hydroxide.

Thionyl chloride reacts with dihydroxydifluoroboric acid, but the reaction is rather slow, even at the boiling point of thionyl chloride (76°). Under the conditions adopted, complete reaction was not realised. Four molecules of thionyl chloride react for every three of dihydroxy-difluoroboric acid consumed. Hydrogen chloride, sulphur dioxide, and boron fluoride are evolved, while the only solid product is metaboric acid :

$$3H_3BO_2F_2 + 4SOCl_2 \longrightarrow 8HCl + 4SO_2 + 2BF_3 + HBO_2$$

The formation of metaboric acid and not boric oxide has a parallel in the reaction with orthoboric acid, only two-thirds of the water of constitution of which reacts with thionyl chloride at the boiling point of the latter :

$$H_3BO_3 + SOCl_2 \longrightarrow HBO_2 + SO_2 + 2HCl$$

Dihydroxydifluoroboric acid liberates much heat with phosphoric oxide in the cold. No boron trifluoride is liberated, even on heating, but hydrogen fluoride is liberated and is immediately converted into silicon tetrafluoride if glass apparatus is employed. Boron phosphate is also formed, according to the scheme :

$$2H_3BO_2F_2 + P_2O_5 \longrightarrow 2BPO_4 + [H_2O] + 4HF$$

The manner of dehydration is thus different from that occurring with sulphuric acid (Sowa et al., loc. cit.), viz. :

$$6H_3BO_2F_2 \longrightarrow B_2O_3 + [9H_2O] + 4BF_3$$

The reason for this is doubtless connected with the formation of the very stable lattice compound, boron phosphate, BPO_4 .

From the foregoing, it is to be noted that the characteristic feature of the reactions of dihydroxydifluoroboric acid with halogenating agents is the ready production of boron trifluoride. With phosphorus compounds the formation of the lattice compound boron phosphate (cf. Schulze, Z. physikal. Chem., 1934, B, 24, 215) was observed, but otherwise most of the boron was obtained finally as the trifluoride. No other simple or mixed halide of boron was formed in any of the reactions, although such were diligently searched for by chemical tests and by vapour-density and vapour-pressure measurements of the fractions obtained from fractional condensation in vacuum-apparatus.

Thus, dihydroxydifluoroboric acid reacts in a number of different ways: $6H_3BO_2F_2$ may alternatively be given the following "reaction formulæ":

(1a)
$$B_2O_3, 4BF_3, 9H_2O$$
 (1b) $2HBO_2, 4BF_3, 8H_2O$ (1c) $2H_3BO_3, 4BF_3, 6H_2O$
(2) $2B_2O_3, 2BF_3, 6HF, 6H_2O$ (3) $3B_2O_3, 12HF, 3H_2O$

Formula (1*a*) represents its mode of reaction with phosphorus pentachloride, phosphorus pentabromide, and concentrated sulphuric acid. The variants (1*b*) and (1*c*), which contain the same amount of boron trifluoride, respectively represent the behaviour with thionyl chloride and certain oxygen-containing organic compounds of low molecular weight, namely, alcohols, esters, ketones, aldehydes, and non-cyclic ethers (Kroeger *et al.*, *loc. cit.*). Formula (2) represents the mode of reaction with phosphorus tri-iodide, and formula (3) that with phosphoric oxide. It follows that no single reaction formula accounts for the general chemical behaviour, indicating that more than one molecular species may be present in the anhydrous acid : many of the reactions, particularly the comparatively ready liberation of boron trifluoride, are more easily explained on the assumption that the acid is to a slight extent in equilibrium with boron trifluoride hydrate on the one hand, and boric acid on the other, *e.g.*:

$$3H_3BO_2F_2 \implies 2BF_{3,2}H_2O + HBO_2$$

$$3H_3BO_2F_2 \implies BF_{3,2}H_2O + BF_{3,}H_2O + H_3BO_3$$

or

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It is relevant that $BF_{3,}2H_{2}O$ is a strong acid and is to be written $[H_{3}O][BF_{3}\cdot OH]$ (Meerwein and Pannwitz, J. pr. Chem., 1934, [ii], 141, 123; Klinkenberg and Ketelaar, Rec. Trav. chim., 1935, 54, 959), but from its behaviour it must be regarded as being partly dissociated into an equilibrium mixture of hydroxyfluoroboric acids (McGrath et al., loc. cit.). Moreover, Wamser (J. Amer. Chem. Soc., 1948, 70, 1209) has observed that the acid H[BF_{3}\cdot OH] is a particularly stable intermediate equilibrium stage in the reaction between boric acid and hydrogen fluoride.

Dihydroxydifluoroboric acid is stated to behave as a strong monobasic acid and the formula

of the dissociated acid has been given as H[HO - B - OH] (or perhaps more correctly, in F - F - Faqueous solution $[H_*O][HO - B - OH]$) as suggested by Sowa *et al.* This representation is

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however not permissible for the anhydrous acid, since this has a conductivity only of the order of that of concentrated sulphuric acid, in which free protons do not occur in the liquid as such but are absorbed into the structure of the acid, as shown by X-ray studies (Finbak, *Tids. Kjemi Bergvesen Met.*, 1943, 3, 40). The suggestion by Kroeger *et al.* that the proton of the dihydroxydifluoroboric acid is co-ordinated to the oxygen (or alternatively to the fluorine), so that

molecules such as $H \xrightarrow{F_1} O \xrightarrow{H} B \xrightarrow{H} O \xrightarrow{H} H$ are present does not do more than partial justice to the $H \xrightarrow{F_1} F$

facts. First, it is very doubtful if single molecules of $H_3BO_2F_2$ are any more capable of independent existence than those of, say, HBF_4 . Secondly, apart from the fact that many compounds containing both hydrogen and fluorine are associated, the presence of the hydroxyl groups would lead one to expect marked association. It is moreover hard to see how hydrogen bonds involving both the oxygen and the fluorine of the various molecular species present could fail to be formed, although the literature does not even mention the possibility of hydrogen bonding in this connexion. That hydrogen bonds do indeed occur is strongly indicated by the physical properties of the anhydrous acid, namely, high viscosity, high density, high boiling point relative to the size of the molecule, and high latent heat of vaporisation. For a compound containing only boron, oxygen, fluorine, and hydrogen, the surprisingly high density of 1.66, which approaches that of orthophosphoric acid, is especially noteworthy, the more so since the a priori possibilities of hydrogen-bond formation are about the same as in phosphoric and sulphuric acids, which dihydroxydifluoroboric acid resembles in viscosity (as well as in electrical conductivity). In both sulphuric and phosphoric acid, as in water, hydrogen bonding is known to lead to an O-H-O distance of 2.85 A. (Finbak, loc. cit.; Bastiansen and Finbak, Tids. Kjemi Bergvesen Met., 1944, 4, 40), and in the case of dihydroxydifluoroboric acid we now have the evidence of the increased stability of the hydroxyl groups and hence reduced reactivity which would arise from quite firm hydrogen bonding. Taken as a whole, the reactions here reported with halogenating agents are remarkably sluggish, while phosphorus trichloride does not react at all under the conditions tried. The hydroxyl groups are thus even less reactive than those in orthoboric acid, which reacts, for instance, with phosphorus trichloride on heating and more readily with thionyl chloride. The results of X-ray studies and Raman spectroscopy are awaited with interest.

Finally, the presence of small amounts of the products of *non-electrolytic* dissociation must be admitted, since the vapour density is almost exactly half that required by the formula $H_3BO_3F_2$ (Sowa *et al.*). It follows that the total pressure of the products of dissociation reaches one atmosphere at 160°, which is therefore not a true boiling point but a dissociation equilibrium temperature. Sowa *et al.* suggest that the molecular species present in the vapour phase are $HF + BF(OH)_2$, but were this the case it is hard to see why the hydrogen fluoride does not attack the glass walls of the distilling apparatus. In fact, dihydroxydifluoroboric acid can be distilled in ordinary glass apparatus without etching, and no decomposition is observed beyond the deposition of a very small amount of an unidentified white solid on the walls of the condenser (cf. Sowa *et al.*, *loc. cit.*). A more probable alternative, therefore, is the equilibrium

$$H_3BO_2F_2 \iff H_2O + BF_2 \cdot OH$$

(liquid) (vapour)

the members on the right-hand side also being able to participate in hydrogen bonding in the liquid phase. Here again there is a parallel with sulphuric acid, for according to the Brønsted-Lowry concept of an acid, the water molecules will pick up protons from further molecules of

the acid and give rise to hydroxonium ions. Since, as in the case of sulphuric acid (Finbak, *Avh. Norske Videnskaps-Akad. Oslo*, I. *Mat.-naturv. Klasse*, 1944, No. 6), the number of protons transferred is limited by the number of water molecules present, and since the conductivity of anhydrous dihydroxydifluoroboric acid is appreciable, it is to be presumed that the forementioned dissociation is not negligible in the liquid phase, even at room temperature.

EXPERIMENTAL.

Preparation of Dihydroxydifluoroboric Acid.—The method mainly adopted was the action of boron trifluoride on orthoboric acid at room temperature, $2BF_3 + 4H_3BO_3 \longrightarrow 3HBO_2 + 3H_3BO_2F_2$. Gaseous boron trifluoride was passed over solid boric acid until the latter became syrupy. On subsequent distillation, dihydroxydifluoroboric acid came over at 160°. The yield was almost 100% based on the boric acid.

An alternative method consisting of separating dihydroxydifluoroboric acid from a reaction mixture of calcium fluoride, boric oxide, and a limited quantity of concentrated sulphuric acid did not prove to be so satisfactory, and in view of the rather poor yield was abandoned.

Redistilled dihydroxydifluoroboric acid had d^{20} 1.6605 (cf. d^{25} 1.6569, d^{30} 1.6539 reported by Sowa et al., loc. cit.; cf. Kroeger et al., loc. cit.).

Reactions of Dihydroxydifluoroboric Acid with Halogenating Agents.—General. In each case, attempts were first made to carry out the reaction at room temperature, heat being applied subsequently. All volatile products were collected, the liquids being condensed by means of a Liebig condenser and substances boiling below room temperature in a liquid-oxygen trap for subsequent examination by high-vacuum technique. The solid residue left in the reaction flask was recovered and investigated, although it was not always possible to identify it completely.

With phosphorus trichloride. Dihydroxydifluoroboric acid (41.6 g.) and phosphorus trichloride (45.8 g.) were mixed. The mixture separated into two layers. No visible reaction occurred in the cold or on heating. The reactants were finally distilled off unchanged, and not more than a trace of hydrogen chloride was collected in the liquid-oxygen trap.

With phosphorus pentachloride. Preliminary experiments, in which excess of phosphorus pentachloride was employed, indicated reactions in equimolecular proportions. The dihydroxydifluoroboric acid was run on to phosphorus pentachloride. A copious evolution of hydrogen chloride occurred in the cold. When the mixture was heated, further hydrogen chloride was evolved and some phosphorus oxychloride distilled. The contents of the liquid-oxygen trap gave positive tests for boron, fluorine, and chlorine.

In the next experiment, dihydroxydifluoroboric acid (24 g.) in slight excess was added to phosphorus pentachloride (47 g.). The excess of acid was subsequently recovered unchanged. The condensate in the liquid oxygen trap was transferred to a vacuum apparatus. Its vapour pressure lay between that of hydrogen chloride (b. p. -85°) and that of boron trifluoride (b. p. -101°). Successive head fractions were pumped off and the vapour density of each measured by Martin and Dial's procedure (J. Amer. Chem. Soc., 1950, 72, 852). The vapour density of the successive fractions dropped from 24.89 to 19.90 (BF₃, 33.9; HCl, 18.25). These experiments indicated a BF₃: HCl molar ratio of approx. I: 4 and demonstrated the absence of heavier and less volatile compounds such as boron trichloride or boron fluorochloride. 24.2 g. of impure phosphorus oxychloride were recovered. The residue was a light-grey powder containing boron and phosphorus but no halogen, insoluble in acids and dilute alkali, but partly soluble in hot concentrated sodium hydroxide solution; in this it behaved like boron phosphate.

With phosphorus pentabromide. Preliminary experiments indicated that the reaction proceeded as with phosphorus pentachloride, except that no appreciable quantity of hydrogen bromide was evolved until heating was commenced. Dihydroxydifluoroboric acid (13 g.) and phosphorus pentabromide (65 g., equimolecular quantity) were warmed until the evolution of gas was complete. Subsequent attempts to distil off the phosphorus oxybromide formed were only partly successful, some remaining with the solid residue. The latter, when washed free from the oxybromide, proved to have the same inert properties as in the case of the experiment with phosphorus pentachloride and was to all appearances boron phosphate. The condensate in the liquid-oxygen trap was mainly hydrogen bromide with a smaller quantity of boron trifluoride. Complete separation was not effected, but, on subsequent fractional condensation in vacuum apparatus, the boron and fluorine collected in the lighter (vapour density, 39-56) and more volatile head fraction, while the tail fraction gave negative tests for both fluorine and boron and behaved as pure hydrogen bromide (vapour density, 40-64). There were no indications of the formation of boron bromide or mixed halides of boron.

With phosphorus tri-iodide. Preliminary experiments indicated that no reaction occurred in the cold but that, on heating, hydrogen iodide was evolved, the molecular ratio of $H_3BO_2F_2$: PI_3 being 3:2. Accordingly, dihydroxydifluoroboric acid (15 g.) was heated with phosphorus tri-iodide (48 g.). The gas evolved proved, on examination in vacuum apparatus, to be a mixture of hydrogen iodide, boron trifluoride, and silicon tetrafluoride. There was an appreciable quantity of the latter, which appeared to have arisen through the secondary attack of hydrogen fluoride on the glass apparatus, which was severely etched. Two very small liquid fractions were obtained. The first (b. p. 76°) (about 0.2 c.c.) was violet through dissolved iodine. The amount was too small to identify. It was denser than water, with which it was immiscible and did not appear to react. It dissolved in sodium hydroxide solution, however, and the resulting solution gave a positive test for boron (as well as for iodine). The second liquid fraction (about 0.5 c.c.) was unchanged dihydroxydifluoroboric acid (b. p. 160°). The solid residue was yellow-brown and contained phosphorus and boron, but no halogen. It smelled of phosphorus, ignited on heating and liberated phosphine on treatment with sodium hydroxide. It could not be identified, but part of it was insoluble and behaved like boron phosphate. It appeared that the elementary phosphorus in the residue was liberated only on strong heating by virtue of a secondary

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reaction, since the residue from the preliminary experiment, which had not been so strongly heated, was light orange and liberated a much smaller proportion of phosphine on treatment with alkali.

With thionyl chloride. Thionyl chloride was purified by distillation over quinoline and linseed oil. In one experiment, the chloride (57·1 g.) and dihydroxydifluoroboric acid (30·0 g.) were mixed. The two liquids separated into two layers and appeared not to react in the cold, but after 12 hours a considerable quantity of condensate had collected in the liquid-oxygen trap. On heating, the reaction proceeded more rapidly, but was still incomplete after 1 hour, during which the unchanged portions were distilled over. The condensate in the liquid-oxygen trap was shown by fractional condensation in vacuum-apparatus to consist of a mixture of boron trifluoride, hydrogen chloride, and sulphur dioxide. The quantities of reactants recovered unchanged were 10·1 g. of thionyl chloride and 6·8 g. of dihydroxy-difluoroboric acid; *i.e.*, 47·0 g. of thionyl chloride had reacted with 23·2 g. of dihydroxydifluoroboric acid, which corresponds approximately to the molecular ratio $4SOCl_2: 3H_3BO_2F_2$. The residue was a white powder (3·8 g.), containing boron, but no sulphur or halogen. It was completely soluble in water giving an acidic solution, a weighed quantity titrating with sodium hydroxide and glycerol as metaboric acid (35·00 g./l. by weight, 35·22 g./l. by titration).

In another experiment it was demonstrated that thionyl chloride at its b. p. (76°) converts orthoboric acid not into metaboric acid, but into boric oxide. Orthoboric acid $(20 \cdot 0 \text{ g.})$ was refluxed with excess of purified thionyl chloride for a considerable period after the evolution of hydrogen chloride and sulphur dioxide had ceased (24 hours in all). After removal of the excess of thionyl chloride and evacuation, metaboric acid (14.2 g.) was obtained (theory, 14.18 g.).

With phosphoric oxide. The quantities of dihydroxydifluoroboric acid and phosphoric oxide used were 84 g. and 71 g. respectively (B: P ratio = 1:1). The liquid dihydroxydifluoroboric acid was added slowly to the oxide. A violent exothermic reaction took place, but no gas was evolved at this stage. On subsequent heating, a white solid collected in the liquid-oxygen trap. The condensate contained fluorine, but no boron or phosphorus, and by its sublimation point, vapour density, and chemical behaviour was proved to be practically pure silicon tetrafluoride, this probably having arisen through the primary liberation of hydrogen fluoride (severe etching). The residue contained boron and phosphorus, but no fluorine. The insoluble portion, after being washed, had the properties of boron phosphate.

The authors thank the Imperial Smelting Company Ltd. for kindly supplying boron trifluoride in cylinders, and one of them (D. D.) is indebted to the Department of Scientific and Industrial Research for a Maintenance Grant.

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[Received, March 6th, 1951.]