Discussion

The results presented in the preceding article[1] indicated that benzoyl peroxide in benzene, following a "preliminary period," decomposed as if two parallel reactions were occurring, a first order and a second order. This decomposition was interpreted as an initial dissociation of the peroxide followed by the further dissociation of the hemimer and the parallel reaction of the hemimer as an oxidizer. The final products of the reaction were determined by the reactions of the hemimer. The almost constant order of reaction with changing environment (Tables I, IV and V) and with halogen substitution on the benzene nucleus (Table VI) indicate a uniform mechanism of decomposition.

If the initial dissociation were ionic, $(RO)_2 = RO^+ + RO^-$, we would expect a large solvent effect on the rate of reaction in relation to the dielectric constant.[3] The increase in the rate of decomposition for a twelve-fold increase in the dielectric constant of the solvent is relatively small (Table V). The temperature coefficient for a reaction involving an ionized substance is usually relatively low.[3] The large variation of the rate constant with temperature and the comparative insensitivity to changes in dielectric constant may be further evidence that the decomposition proceeds via an uncharged radical mechanism, as was previously advanced[4,1] and is now accepted by many workers in the field.

The degree of the initial dissociation may be determined in part by the relative "negativity" of the radicals R and R′ of the peroxide R–O–O–R′ exactly as found by Gomberg[5] for the formation of trivalent carbon. The rate of reaction of the peroxide is determined by the degree of the dissociation which precedes and thus controls the subsequent rate determining reactions. Of those studied *o*-chlorbenzoyl peroxide decomposes the most rapidly. The rate constants for the *o*- and *p*-chlorobenzoyl peroxides have approximately the same ratio as the ionization constants of the two chlorobenzoic acids (Table VI), but no such simple relationship is found among the corresponding constants in the unsubstituted, *p*-chloro and *m*-bromo derivatives.

The data are correlated by the postulate that the initial reaction is a simple dissociation of the peroxide with the formation of radicals which contain monovalent oxygen as a constituent followed by two parallel reactions. The products of the decomposition are determined by these parallel reactions.

Summary

The rates of decomposition of benzoyl peroxide in benzene and the order of reaction at two temperatures are reported.

A study of the relation of the rate of reaction and order of reaction to the dielectric constant of the solvent was made.

The effect of substitution on the benzene nucleus of the benzoyl peroxide was studied.

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[3] Walden, *Z. physik. Chem.*, **54**, 129 (1905), and later.

[4] Hey and Waters, *Chem. Rev.*, **21**, 169 (1937).

[5] Gomberg, *ibid.*, **1**, 91 (1924).

[CONTRIBUTION FROM THE LABORATORY OF C. A. WAMSER]

Hydrolysis of Fluoboric Acid in Aqueous Solution

BY CHRISTIAN A. WAMSER

Aqueous fluoboric acid, which is now commercially available in the form of a 40% concentrate, is prepared[1] by treating aqueous hydrofluoric acid with the calculated amount of boric acid according to the equation

$$4HF + H_3BO_3 = HBF_4 + 3H_2O$$

It has been well known that aqueous solutions of fluoboric acid are more or less strongly hydrolyzed depending on the dilution, temperature and length of time they have been standing after preparation. Such solutions always contain more H ion than can be accounted for by the fluoboric acid they are calculated to contain.

Any successful explanation of the net changes occurring on hydrolysis must be capable of accounting for the following experimentally observable facts:

(1) When four moles of hydrofluoric acid and one mole of boric acid are mixed in aqueous medium, an immediate sharp increase in conductance occurs and heat is evolved, yet the solution contains no fluoboric acid immediately after the preparation (no precipitate with nitron). The total titratable acidity (as measured by the volume of standard alkali consumed to the phenolphthalein end-point in the presence of mannitol) of such a mixture immediately after preparation corresponds to five equivalents of acid, the solution at the end-point containing only F^- and BO_2^- anions.

(2) After preparation, the fluoboric acid content gradually increases to a final (equilibrium) value, while the total acidity decreases to a definite value. The only anions present at the titration end-point are BF_4^-, F^- and BO_2^-.

(3) When a fluoboric acid concentrate (which is itself appreciably hydrolyzed) is diluted with water, the total acidity gradually increases to a final (equilibrium) value.

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[1] F. Fischer and K. Thiele, *Z. anorg. Chem.*, **67**, 304 (1910).

According to Wilke-Dörfurt and Balz[2] the fluoborate ion hydrolyzes

$$BF_4^- + 3H_2O \rightleftharpoons H_3BO_3 + 3H^+ + 4F^-$$

so that a hydrolyzed solution contains hydrofluoric and boric acids as well as fluoboric acid. Assuming this reaction, Ryss and Bakina[3] have determined the hydrolysis constant from *p*H data. It has been found, however, that except in the case of very dilute solutions, hydrolyzed aqueous fluoboric acid solutions probably do not contain any free boric acid because the addition of mannitol to such solutions does not result in any increase in conductance.

According to Travers and Malaprade[4] hydrofluoric acid and boric acid react immediately to form a fluoboric acid, not HBF_4, and the latter is only formed slowly at the expense of the first-formed complex until finally an equilibrium between the two acids is reached.

It will be shown herein that when 4HF and H_3BO_3 are mixed in aqueous solution an immediate reaction occurs and HBF_3OH is formed. This is followed by a slower reaction involving this first-formed complex and hydrofluoric acid and resulting in the formation of fluoboric acid

(1) $H_3BO_3 + 3HF \longrightarrow HBF_3OH + 2H_2O$ (very fast)
(2) $HBF_3OH + HF \rightleftharpoons HBF_4 + H_2O$ (slower)

Reaction (2) continues until finally a state of equilibrium is reached.

The Reaction $H_3BO_3 + 3HF \rightarrow HBF_3OH + 2H_2O$.—If an aqueous solution of boric acid is titrated conductometrically with hydrofluoric acid, it will be found that the conductance increases sharply until the point representing the addition of between three and four moles of hydrofluoric acid per mole of boric acid has been reached; further additions of hydrofluoric acid cause a much more gradual increase. Figure 1 is a plot of such a titration and the data for it were obtained as follows:

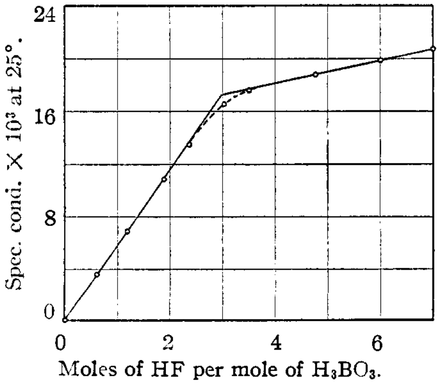

Fig. 1.—Conductance of H_3BO_3–HF mixtures immediately after preparation.

For each point on the curve a separate mixture was made up by treating a solution containing a fixed amount of recrystallized boric acid with a measured volume of a standard hydrofluoric acid solution in a calibrated polystyrene volumetric bottle at 25°. Immediately after preparation the mixture was transferred to a polystyrene conductance cell. The concentration of boric acid in each case was 0.0522 *M*.

Figure 1 is the plot of the conductance of the mixtures against the number of moles of hydrofluoric acid added per mole of boric acid. The well-defined break corresponds to a ratio of 3 to 1, and the reaction is probably

$$H_3BO_3 + 3HF \longrightarrow HBF_3OH + 2H_2O$$

Boric acid here behaves as a base analogous to aluminum hydroxide

$$Al(OH)_3 + 3HF \longrightarrow AlF_3 + 3H_2O$$

The acid HBF_3OH is known in the anhydrous state (Meerwein's acid, $BF_3{\cdot}H_2O$)[5] and probably does not exist in aqueous solutions except in equilibrium with fluoboric acid. It is apparently able to form salts, for, as will be shown, KBF_3OH may be easily prepared.

The conductance plot of Fig. 1 indicates that HBF_3OH is a strong acid, although its specific conductance at this concentration (0.0522 *M*) is 17.3×10^{-3} at 25° compared with 20.3×10^{-3} for fluoboric acid at this same concentration (corrected for hydrolysis from data presented in a later section). HBF_3OH is hence somewhat weaker than fluoboric acid.

The reaction deduced from the previous data is probably oversimplified; it does not represent all the important changes that can take place, and the following may also occur

$H_3BO_3 + HF \longrightarrow HBF(OH)_3$ (rapid)
$HBF(OH)_3 + HF \longrightarrow HBF_2(OH)_2 + H_2O$ (rapid)
$HBF_2(OH)_2 + HF \longrightarrow HBF_3OH + H_2O$ (rapid)

If HBF_3OH were the only acid formed immediately after boric acid and hydrofluoric acid are mixed, it would be expected that the specific conductance of the mixture $H_3BO_3 + 3HF$ would be 17.3×10^{-3} (the intersection of the lines of Fig. 1). Actually about 3.3 moles of hydrofluoric acid per mole of boric acid are required to give this conductance and this seems to indicate that a weaker acid is in rapid reversible equilibrium with HBF_3OH, and present in appreciable amount. It is therefore possible that appreciable amounts of $HBF_2(OH_2)$ (probably a slightly weak acid) and $HBF(OH)_3$ (probably weak) exist in rapid reversible equilibrium with boric acid, hydrofluoric acid and HBF_3OH. The acid $HBF_2(OH)_2$ is in fact known in the anhydrous state (dihydroxyfluoboric acid[6]). The author has also prepared a salt from concentrated solutions of equimolar proportions of potassium bifluoride and boric acid which has a

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(2) E. Wilke-Dörfurt and G. Balz, *Z. anorg. allgem. Chem.*, **159**, 197 (1926).

(3) J. G. Ryss and N. P. Bakina, *Compt. rend. l'acad. Sci. U. S. S. R.* (N. S.), **2**, 107 (1936).

(4) A. Travers and L. Malaprade, *Bull. soc. chim.*, **47**, 788 (1930).

(5) H. Meerwein, *Ber.*, **66B**, 411 (1933).

(6) F. J. Sowa, J. W. Kroeger and J. A. Nieuwland, THIS JOURNAL, **57**, 454 (1935).

ratio of K:B:F of 1:1:2 and the analysis of which corresponds closely to $KBF_2(OH)_2$. The salt further gives a well-defined X-ray diffraction pattern different from potassium fluoborate and KBF_3OH.

Preparation of Potassium Hydroxyfluoborate (KBF_3OH).—In their attempts to identify the first-formed complex acid in $4HF-H_3BO_3$ mixtures in aqueous solution, Travers and Malaprade[4] isolated a salt from cold, concentrated mixtures of potassium bifluoride and boric acid. Their chemical analyses of this salt indicated a ratio of K:B:F of 1:1:3 and they ascribed to it the formula $K_2B_2F_6 \cdot 1.5H_2O$. They found that the salt hydrolyzes readily and that the volume of standard alkali consumed by an aqueous solution of it up to the phenolphthalein end-point (in the presence of mannitol) corresponded closely to that calculated to decompose it to fluoride and metaborate.

This salt is, however, probably KBF_3OH, produced in accordance with the following equation, which also explains the increase in alkalinity that occurs when strong solutions of potassium bifluoride are treated with boric acid

$$2KHF_2 + H_3BO_3 \longrightarrow KBF_3OH + KF + 2H_2O$$

Travers and Malaprade[4] do not offer an equation to explain the formation of their salt, for no simple reaction (not involving an oxidation or reduction) presented itself.

Several samples of KBF_3OH were prepared as follows: 100 grams of potassium bifluoride was dissolved in 250 ml. of water in a polystyrene beaker. After standing for several hours at room temperature, the solution was freed from potassium fluosilicate and undissolved potassium bifluoride by filtering through paper in a polystyrene funnel. The solution, in polystyrene, was placed in an ice-water-bath and 40 g. of powdered boric acid added with continual stirring. The boric acid dissolved readily and within an hour, during which time the solution was occasionally stirred, small crystals deposited. These were filtered off on a sintered glass funnel (this liquor has a *p*H of about 6 and does not attack glass appreciably), washed sparingly with ice-water, then with larger amounts of 95% ethanol and acetone and dried at 120°. The analysis of two lots of crystals thus obtained is given in Table I.

TABLE I

ANALYSIS OF CRYSTALS OBTAINED FROM $2KHF_2 + H_3BO_3$

	Theoretical for KBF_3OH	Theoretical for $K_2B_2F_6 \cdot 1^1/_2 H_2O$	Lot 1	Lot 2
% K[a]	31.56	32.47	31.85	31.68
% B[b]	8.73	8.98	8.90	8.81
% F[c]	46.00	47.34	45.82	46.10
Milli-eq. weight[d]	0.0413	0.0401	0.0410	0.0411

[a] By repeated evaporation with sulfuric acid in platinum crucible and ignition to potassium sulfate. [b] By methyl alcohol distillation method of Chapin. [c] By lead chlorofluoride method. [d] Weight of a sample divided by the number of ml. of 1 *N* sodium hydroxide required to the phenolphthalein endpoint (in presence of mannitol).

The product obtained by the method described above and that obtained by following the directions of Travers and Malaprade[4] give identical X-ray diffraction patterns.

The salt KBF_3OH is distinguished from potassium fluoborate as follows: (1) The hydroxyfluoborate is much more soluble in water. (2) An aqueous solution of the hydroxyfluoborate gives no precipitate with nitron acetate. (3) An aqueous solution of the hydroxyfluoborate hydrolyzes readily in the presence of alkali, at room temperature: ($KBF_3OH + 3KOH \rightarrow 3KF + KBO_2 + 2H_2O$, while salts of fluoboric acid hydrolyze only very slowly in the presence of alkali (rapidly only at the boiling point and in the presence of excess calcium ions[7]).

The ease with which KBF_3OH decomposes in the presence of alkali explains why a mixture of $4HF + H_3BO_3$ immediately after preparation and though a reaction has taken place, requires five equivalents of alkali in a titration of total acidity and why the only anions present at the end-point are F^- and BO_2^-.

It was also found that KBF_3OH may be fused without suffering any decomposition or loss in weight, a property which would not be expected of a hydrate of the form assumed by Travers and Malaprade.[4]

Attempts to recrystallize the hydroxyfluoborate from aqueous solutions were unsuccessful, the product obtained being contaminated with fluoride and boric acid (extractable with ether-alcohol).

The Reaction $HBF_3OH + HF \rightarrow HBF_4 + H_2O$.—This reaction is slow enough, at concentrations of the order of 0.1 *M* at 25°, to permit of accurate estimation of the acids present based on total acidity, from which the amount of fluoboric acid formed can be easily calculated and the kinetics of the reaction studied. That the total acidity may be used for calculating the proportion of the three acids present has been proved over a wide range of concentration by the comparison of fluoboric acid concentrations thus calculated with direct gravimetric determinations of fluoboric acid as nitron fluoborate, as will be indicated in a later section.

For studying the kinetics of $HBF_3OH + HF \rightarrow HBF_4 + H_2O$, the reaction mixture is conveniently prepared from four moles of hydrofluoric acid and one mole of boric acid. Immediately after preparation, *i. e.*, at time $t = 0$, the total acidity is equal to five times that theoretically equivalent to the (stoichiometrically possible) fluoboric acid. If this latter calculates to T_1 and the observed titration at any time t is T_2, then the fraction of the possible fluoboric acid which is actually present at that time is $(5T_1 - T_2)/4T_1$.

The kinetics of this reaction was investigated at 25° at a concentration of 0.1105 *M* by mixing a solution of 3.805 g. of pure boric acid and one con-

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(7) A. Gonard, *Bull. soc. chim.*, **9**, 917 (1942).

taining 4.922 g. of hydrogen fluoride in a calibrated polystyrene bottle (volume at mark 556.8 ml.) which was allowed to remain suspended in a thermostat bath. At recorded intervals of time, aliquots of the mixture were removed and quickly titrated for total acidity. Table II contains the data for this reaction. T_1 is here 2.62 ml. and the final (equilibrium) value of T_2 = 4.07 ml. indicates that at this concentration there is present, at equilibrium, 86.2% of the stoichiometrically possible fluoboric acid (or that the solution is hydrolyzed to the extent of 13.8% when the reaction is considered in the reverse direction). When the mixture had come to equilibrium, an aliquot was analyzed directly for fluoboric acid by precipitation with nitron acetate, using essentially the procedure described by Lange[8] except that the precipitate was filtered off within five minutes. There was obtained, from 25 ml. of the mixture, 0.9515 g. of $C_{20}H_{16}N_4 \cdot HBF_4$, corresponding to 86.1% of the total possible fluoboric acid.

TABLE II

KINETICS OF $HBF_3OH + HF \rightarrow HBF_4 + H_2O$ AT 25°

t = time in minutes. T_1 = 2.62 (ml. 1.054 N NaOH) per 25 ml. aliquot. T_2 = observed titration (ml. 1.054 N NaOH $\Leftrightarrow$ total acidity). a = initial concn. of HBF_3OH (and HF) in moles/liter = 0.1105. x = concn. of HBF_3-OH (or HF) reacting in time t.

t	T_2	%HBF_4 formed = $(5T_1 - T_2)/4T_1$ × 100	$K_1 = \frac{1}{t}\frac{x}{a(a-x)}$
0	(13.10)	(0)	
8.5	10.32	26.5	0.382
16.5	8.72	41.8	.394
24	7.75	51.0	.392
32	6.98	58.4	.397
41	6.38	64.1	.394
52	5.85	69.2	.390
72	5.26	74.8	.372
103	4.77	79.5	.340
163	4.36	83.4	.280
218	4.19	85.0	.236
equil.	4.07	86.2	

The last column of Table II lists values of a specific reaction rate calculated on the basis of the reaction being of second order. The average value of K_1 obtained from the earlier part of the reaction is 0.392 liters moles^{-1} min.$^{-1}$ at 25°.

The Reaction $HBF_4 + H_2O \rightarrow HBF_3OH + HF$.—This reaction represents the hydrolysis of fluoboric acid in aqueous solution, and its kinetics were investigated at the same concentration (0.1105 M) as the reverse reaction considered in the previous section. The reaction mixture was prepared from equivalent quantities of barium fluoborate dihydrate and sulfuric acid: $Ba(BF_4)_2 + H_2SO_4 \rightarrow 2HBF_4 + BaSO_4$. This device was used by Travers and Malaprade[4] in their studies of solutions containing fluoboric acid free from its hydrolysis products.

Pure barium fluoborate dihydrate was prepared by the method of Funk and Binder[9] and analyzed as follows: Calcd. for $Ba(BF_4)_2 \cdot 2H_2O$: Ba, 39.59; BF_4, 50.04. Found: Ba, 39.65; BF_4, 49.66 (BF_4 by nitron method). The kinetics of this hydrolysis reaction was investigated as follows:

A solution of 10.675 g. of $Ba(BF_4)_2 \cdot 2H_2O$ in water was mixed with a solution containing 59.27 ml. of 1.038 N H_2SO_4 in the polystyrene bottle mentioned previously. The mixture was maintained at 25° in a thermostat bath and aliquots were withdrawn at recorded intervals of time. Total acidity was determined by titration in the usual manner. The precipitated barium sulfate was not removed since it is inert with respect to the hydrolysis reaction and to the titrations. The degree of hydrolysis at any time t will be $(T_2 - T_1)/4T_1$, the symbols having the same significance as in the case of the reverse reaction. Here T_1 is 4.87 ml. and the final (equilibrium) value of T_2 = 7.53 ml. indicates a degree of hydrolysis of 13.7% which is in good agreement with the result obtained from the measurements of the equilibrium approached from the opposite direction.

Table III contains the data obtained and the last column lists a specific rate calculated on the basis of the reaction being of first order. The average value of K_2 obtained from the earlier part of the reaction is 0.00090 min.$^{-1}$ at 25°.

The ratio $K_2/K_1 = 2.3 \times 10^{-3}$ thus represents the equilibrium constant for the hydrolysis of fluoboric acid: $HBF_4 + H_2O \rightleftarrows HBF_3OH + HF$ at 25°.

TABLE III

KINETICS OF $HBF_4 + H_2O \rightarrow HBF_3OH + HF$ AT 25°

t = time in minutes. T_1 = 4.87 (ml. 0.5680 N NaOH) per 25 ml. aliquot. T_2 = observed titration (ml. 0.5680 N NaOH $\Leftrightarrow$ total acidity). a = initial concn. of HBF_4 in moles/liter = 0.1105. x = concn. of HBF_4 reacting in time t.

t	T_2	%Hydrolysis = $(T_2 - T_1)/4T_1$ × 100	$K_2 = \frac{1}{t}\ln\frac{a}{a-x}$
0	(4.87)	(0)	
8	5.01	0.72	0.00090
13	5.10	1.18	.00091
20	5.22	1.80	.00091
31	5.40	2.72	.00089
43	5.59	3.70	.00088
60	5.85	5.02	.00087
94	6.28	7.23	.00080
147	6.87	10.27	.00074
206	7.23	12.1	.00063
equil.	7.53	13.7	

TABLE IV

EFFECT OF CONCENTRATION ON THE RATE CONSTANTS K_1 AND K_2

Concn. in moles/liter	K_1 at 25°	K_2 at 25°	K_2/K_1
0.0130	0.0823	0.00019	2.31×10^{-3}
.0561	.244	.00055	2.25×10^{-3}
.1105	.392	.00090	2.30×10^{-3}

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[8] W. Lange, *Ber.*, **59B**, 2107 (1926).

[9] H. Funk and F. Binder, *Z. anorg. allgem. Chem.*, **155**, 327 (1926).

TABLE V

DEGREE OF HYDROLYSIS OF AQUEOUS FLUOBORIC ACID SOLUTIONS AT EQUILIBRIUM; TEMP. 25°

A = from 38.04% HBF_4 concentrate and water. B = from 4HF and H_3BO_3. C = from $Ba(BF_4)_2$ and H_2SO_4.

Concn. in moles/liter	Method of prep.	Sample taken, ml. or g.	Titration, ml. std. NaOH or grams $C_{20}H_{16}N_4 \cdot HBF_4$	Hydrolysis %	$\frac{[HBF_3OH][HF]}{[HBF_4]}$
0.001018	A	50 ml.	9.90 of 0.0211 *N*	77.7	2.75×10^{-3}
.00509	A	50	6.88 of 0.1054 *N*	46.3	2.04×10^{-3}
.01018	A	50	4.67 of 0.2634 *N*	35.5	1.98×10^{-3}
.01296	B	25	3.53 of 0.2108 *N*	32.5	2.02×10^{-3}
.02036	A	50	7.97 of 0.2634 *N*	26.6	1.95×10^{-3}
.02036	A	100	0.6003 g.	26.3	1.90×10^{-3}
.0504	A	50	4.19 of 1.054 *N*	18.8	2.20×10^{-3}
.0504	A	50	0.8212 g.	18.6	2.15×01^{-3}
.0527	B	50	4.32 of 1.054 *N*	18.2	2.14×10^{-3}
.0561	A	50	4.50 of 1.054 *N*	17.3	2.02×10^{-3}
.1018	A	50	7.54 of 1.054 *N*	14.1	$2.35 = 10^{-3}$
.1018	A	25	0.8758 g.	14.1	2.35×10^{-3}
.1105	B	25	4.07 of 1.054 *N*	13.8	2.42×10^{-3}
.1105	C	25	7.53 of 0.5680 *N*	13.7	2.38×10^{-3}
.2850	A	50	10.43 of 0.9577 *N*	10.0	3.15×10^{-3}
.2850	A	10	1.0238 g.	10.1	3.23×10^{-3}
.557	A	50	13.95 of 2.634 *N*	8.01	3.95×10^{-3}
.557	A	5	1.0265 g.	7.95	3.76×10^{-3}
5.41	(concentrate)	4.123 g.	8.28 of 2.634 *N*	5.53	17.6×10^{-3}
5.41	(concentrate)	0.5881	0.9636 g.	5.47	17.6×10^{-3}

The specific reaction rates K_1 and K_2 have also been determined at other concentrations using the experimental methods previously described.

The variation of K_1 and K_2 with concentration may be in part an ionic strength effect and in part a result of the hydrogen ion concentration change which simultaneously takes place.

It has been observed that an increase in hydrogen ion concentration (such as occurs for example if hydrochloric acid be added to the reaction mixture $HBF_3OH + HF$) results in an increase in the specific rate K_1. This explains why KBF_4 is rapidly precipitated from the reaction mixture $[2KHF_2 + H_3BO_3 \rightarrow KBF_3OH + KF + 2H_2O]$ on acidification with, say, hydrochloric acid.

Degree of Hydrolysis of Aqueous Fluoboric Acid Solutions.—The degree of hydrolysis of aqueous fluoboric acid solutions (at equilibrium) was determined over the concentration range 0.001 *M* to 5.41 *M* at 25° by diluting weighed amounts of a fluoboric acid concentrate with water. These solutions were stored in sealed polyethylene bottles for three months (a 0.001 *M* solution requires about two months to come to equilibrium), and then suspended in a thermostat bath at 25° for a day. Appropriate aliquots were withdrawn and titrated with standard alkali for total acidity. In those cases where a blank on the mannitol used was significant, it was carefully determined and deducted.

Table V lists the concentration of the solution (always with respect to stoichiometrically possible fluoboric acid), the method of preparation, and the analytical data on which the degree of hydrolysis is based.

Equilibrium constants calculated from the degree of hydrolysis are listed in the final column of Table V. The assumption is here made that the HBF_3OH is itself not appreciably hydrolyzed and therefore $[HF] = [HBF_3OH]$. An examination of these values shows that only that calculated for the most dilute solution measured is appreciably different from the average of the next nine (2.04×10^{-3}). This figure is in good agreement with the constant derived from rate data. At the higher concentrations, the values in the final column increase rapidly, due probably to the increasing difference between activity and concentration as the latter increases.

If the hydrolysis of HBF_3OH proceeds according to $HBF_3OH + H_2O \rightleftarrows HBF_2(OH)_2 + HF$, and the constant is of the same order of magnitude as that for the hydrolysis of fluoboric acid, the amount of $HBF_2(OH)_2$ will be significant only in very dilute solutions. The equilibrium constant would have to be modified from

$$\frac{A \times A}{HBF_4} = \frac{A^2}{HBF_4}$$

where $A = [HF] = [HBF_3OH]$ to

$$\frac{(A + X)(A - X)}{HBF_4} = \frac{A^2 - X^2}{HBF_4}$$

where X = the decrease of $[HBF_3OH]$ due to its hydrolysis = the increase of [HF]. The effect of ignoring the hydrolysis of HBF_3OH is to neglect the X^2 term, and since X is probably of the order of 10^{-3}, the value of the constants as previously calculated will not be appreciably affected until A is of the order of 3×10^{-3}.

Conductometric and *p*H Titrations of Hydrolyzed Fluoboric Acid Solutions.—Several hydrolyzed fluoboric acid solutions were titrated conductometrically and potentiometrically, and in the case of the former method, comparison was made with (a) unhydrolyzed fluoboric acid solution and (b) a solution prepared from salts of the three acids involved.

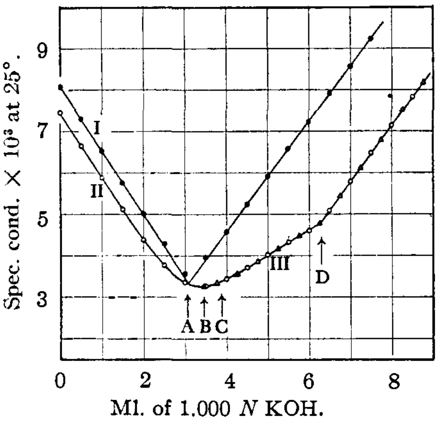

Fig. 2.—Conductometric titrations of aqueous fluoboric acid solutions: I, ●, unhydrolyzed HBF_4 solution; II, ○, hydrolyzed HBF_4 solution; III, △, solution of KBF_4 + KBF_3OH + KHF_2.

Figure 2 summarizes graphically the results of three conductometric titrations: I. The titration of 150 ml. of 0.02036 *M* fluoboric acid (prepared from barium fluoborate and sulfuric acid and titrated immediately after preparation) with 1.000 *N* potassium hydroxide. II. The titration of 150 ml. of 0.02036 *M* fluoboric acid solution at equilibrium, with 1.000 *N* potassium hydroxide. This curve shows the effect of the hydrolysis products on the titratable acidity, the end-point having been displaced from 3.08 to 6.30 ml. This titration (point D on curve II of Fig. 2) corresponds to 26.6% hydrolysis. The point *A* = 3.06 ml. corresponds to the neutralization of the strong acids fluoboric acid and HBF_3OH and very nearly coincides with the end-point of titration I, indicating that the conductance of potassium fluoborate is not appreciably changed by the replacement of a large part of it with an equivalent amount of KBF_3OH (neglecting the conductance of the relatively weak hydrofluoric acid which is present at the point A). It was also found that in this case and in the case of other titrations of fluoboric acid solutions (at equilibrium) at various concentrations, the point of minimum conductance corresponds very closely to the stage of the titration at which KBF_4, KBF_3OH and KHF_2 are present in solution, *i. e.*, point B on curve II. The segment CD = 2.43 ml. which represents the decomposition of KBF_3OH, was found to be a straight line at various concentrations.

III. It was found that the last part of curve II (BD) could be exactly reproduced by titrating a solution containing 0.283 of KBF_4, 0.100 g. of KBF_3OH, and 0.0312 g. of KHF_2 dissolved in water and diluted to the volume of the solution corresponding to this point (B) on curve II (*i. e.*, 153.5 ml.). This is evidence of the correctness of the assumed hydrolysis reaction.

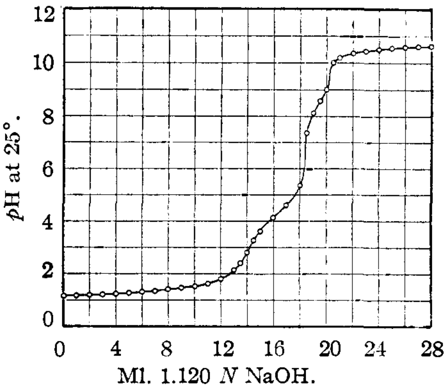

Fig. 3.—pH titration of 100 ml. of 0.1512 *M* fluoboric acid at equilibrium.

Figure 3 represents a *p*H titration of 100 ml. of 0.1512 *M* fluoboric acid at equilibrium (hydrolysis 12.4%) with 1.120 *N* sodium hydroxide at 25°. The first inflection corresponds closely to the neutralization of HBF_4 + HBF_3OH, the second to the stage of the titration corresponding to the decomposition of the $NaBF_3OH$ to sodium fluoride and boric acid, and the final inflection to the total acidity. It is interesting to note here that when a hydrolyzed fluoboric acid solution is treated with iodate–iodide mixture as in the standard iodimetric determination of acidity, the iodine liberated is equivalent to the second inflection in the *p*H curve.

This *p*H titration was performed in a polystyrene beaker using glass and calomel electrodes and although this cell combination may not be well suited to such a titration, it enables the measurements to be extended over the desired range.

Effect of Excess Boric Acid or Hydrofluoric Acid on the Hydrolysis Equilibrium.—A series of solutions containing the same concentration of fluoboric acid concentrate but various amounts of added excess boric or hydrofluoric acid were allowed to come to equilibrium at 25° in sealed polyethylene bottles. Total acidity was determined on appropriate aliquots and after correcting for the known added amount of either acid, the remaining titration was considered as due to fluoboric acid and its hydrolysis products and the degree of hydrolysis so calculated. Some of the solutions were also analyzed directly, by the nitron method, for fluoboric acid.

Figure 4 is a plot of the degree of hydrolysis of a 0.0527 *M* HBF_4 solution against the indicated concentrations of added boric or hydrofluoric acid. Excess hydrofluoric acid markedly decreases the hydrolysis while boric acid increases the equilibrium ratio of HBF_3OH to fluoboric acid.

Conductance of Aqueous Fluoboric Acid Solutions.—The conductances at 25° of aqueous solutions of fluoboric acid were measured in polystyrene cells over the concentration range 0.005 to 0.1 *M*. The curves of Fig. 5 were plotted from measurements made on the following

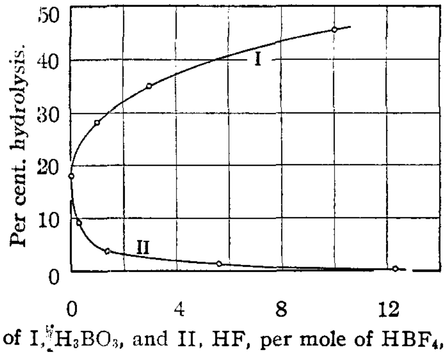

Fig. 4.—Influence of added excess H_3BO_3 and HF on the degree of hydrolysis (at equilibrium) at 25°.

solutions: I. Mixtures of equivalent amounts of barium fluoborate and sulfuric acid immediately after preparation. II. Aqueous fluoboric acid solutions at equilibrium. III. Mixtures of four moles of hydrofluoric acid and one mole of boric acid immediately after preparation. A curve of the conductance of 4HF has been included for comparison (IV).

The measurements from which curve I was obtained are uncorrected for the barium sulfate contained or for any adsorption or other possible effects caused by its presence in the solutions.

It was found that the addition of pure recrystallized mannitol did not appreciably alter the conductance of any of the solutions, indicating that no appreciable amount of free boric acid was present.

Acknowledgment.—The author acknowledges his indebtedness to Thomas L. Allen of the California Institute of Technology for helpful suggestions.

Summary

Conductance measurements show that when four moles of hydrofluoric acid and one mole of boric acid are mixed in aqueous solution, three moles of the hydrofluoric acid react immediately with the boric acid to form HBF_3OH.

HBF_3OH then reacts more slowly with hydrofluoric acid to form fluoboric acid until an equilibrium is reached.

The kinetics of the reaction $HBF_3OH + HF \rightleftarrows HBF_4 + H_2O$ was measured (1) from left to right (second order), and (2) from right to left (first order).

The equilibrium constant at 25° for the hydrolysis of fluoboric acid in aqueous solution is about 2.3×10^{-3}.

The salt KBF_3OH was prepared from $2KHF_2$ and boric acid and is the same as that reported by Travers and Malaprade[4] as $K_2B_2F_6 \cdot 1^1/_2H_2O$.

The degree of hydrolysis of aqueous fluoboric acid solutions at equilibrium at 25° has been determined over the range 0.001 to 5.41 *M*.

The conductance of aqueous fluoboric acid solutions at 25° has been determined over the range 0.005 to 0.1 *M* for the cases (1) no hydrolysis, (2) equilibrium hydrolysis and (3) complete hydrolysis.

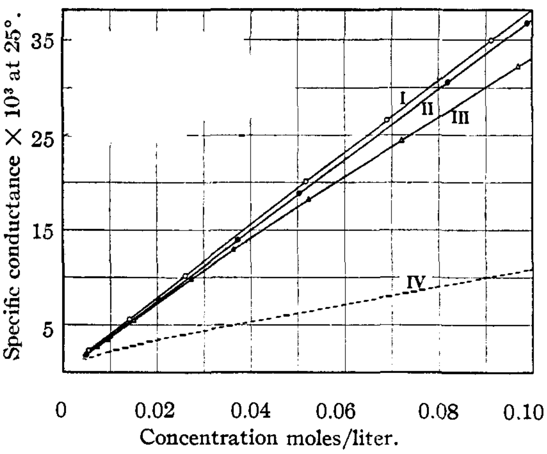

Fig. 5.—Conductance of aqueous fluoboric acid solutions: I, ○, no hydrolysis; II, ●, equilibrium hydrolysis; III, △, complete hydrolysis; IV, ----, 4 HF.

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