TABLE II

THE EQUILIBRIUM CONSTANT FOR $BF^-_4 \rightleftarrows F^- + BF_3$ FROM MEASUREMENTS ON ADDING BORON TRIFLUORIDE TO POTASSIUM FLUORIDE SOLUTIONS AT 20.0°

| $BF_3$, *m* | Equiv. conductance | Equilibrium constant |
|---|---|---|
| | $m_{KF}$ = 0.0512 | |
| 0 | 393 | .... |
| .0106 | 375.5 | 0.018 |
| .0228 | 355 | .010 |
| .0421 | 321 | .0045 |
| .0532 | 303.5 | .0021 |
| .0609 | 303 | .0035 |
| | Mean | 0.0076 |
| | $m_{KF}$ = 0.103 | |
| 0 | 346 | .... |
| .0120 | 335 | 0.0115 |
| .0263 | 323 | .0095 |
| .0410 | 308 | .0023 |
| .0531 | 298 | .0031 |
| .0685 | 288 | .0053 |
| .0785 | 278 | .0031 |
| .0925 | 264.5 | .0014 |
| .105 | 257 | .0012 |
| .115 | 257 | .0023 |
| | Mean | 0.0044 |

Each set of experiments reported in Table II was made at constant ionic concentration since the addition of boron trifluoride merely changed the fluoride ion into fluoborate ion so that the trend in the values for the equilibrium constants can only be attributed to our neglect of the contribution of other equilibria such as the autoprotolysis of the solvent and the interaction of the boron trifluoride with the solvent or lack of precision of the conductance data due to traces of water. However, it is encouraging to note that two independent methods of calculation give the same order of magnitude for reaction 2.

In a third paper, the few results at hand on the interaction of boron trifluoride with hydrofluoric acid alone will be reported.

## Experimental

The experimental procedure has been described in detail elsewhere.[4]

The potassium fluoride was prepared for use by drying $KF \cdot 2H_2O$ overnight in a waxed bottle in a desiccator under high vacuum. The salt was then ground rapidly in an agate mortar to a fine powder and dried again for several days. The potassium fluoborate obtained from Baker and Adamson was dried by the same procedure.

CHICAGO 16, ILLINOIS

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF ILLINOIS INSTITUTE OF TECHNOLOGY]

# The Conductance and Vapor Pressure of Boron Trifluoride in Anhydrous Hydrofluoric Acid[1,2]

BY MARTIN KILPATRICK[3] AND FRED E. LUBORSKY

RECEIVED JUNE 7, 1954

The vapor pressure and conductance in liquid anhydrous hydrofluoric acid have been determined for boron trifluoride over a concentration range of 0.002 to 0.8 molar. The equilibrium $BF_3 + 2HF \rightleftarrows H_2F^+ + BF_4^-$ has been postulated and the equilibrium constant calculated as a function of the concentration. The ion product of the solvent hydrofluoric acid has been estimated to be less than $2 \times 10^{-10}$.

In this solvent the autoprotolysis reaction is $HF + HF \rightleftarrows H_2F^+ + F^-$ (or $HF_2^-$) and boron trifluoride displaces the equilibrium to the right by the reaction $BF_3 + F^- \rightleftarrows BF_4^-$. Boron trifluoride can therefore be regarded as a co-acid and it would be of interest to determine a corresponding equilibrium constant for this last reaction, using other fluorides such as $SbF_5$, $AsF_5$, etc., instead of $BF_3$.

When boron trifluoride dissolves in liquid anhydrous hydrogen fluoride two reactions are possible, the reaction with hydrogen fluoride to form the acid $HBF_4$ which reacts further with the solvent to give the solvated proton and fluoborate ion

$$\underset{\text{dissolved}}{BF_3} + HF \rightleftarrows (HBF_4) + HF \rightleftarrows H_2F^+ + BF_4^- \quad (1)$$

or the boron trifluoride may react with the fluoride ion from the autoprotolysis of the solvent

$$HF + HF \rightleftarrows H_2F^+ + F^- (\text{or } HF_2^-) \quad (2)$$

$$F^- + BF_3 \rightleftarrows BF_4^- \quad (3)$$

If the concentration of $HBF_4$ is small or non-existent, the over-all equilibrium is the same in both cases

$$BF_3 + HF \rightleftarrows H_2F^+ + BF_4^- \quad (4)$$

and quite analogous to the reaction of $CO_2$ and water, where the equilibrium between carbonic acid and the hydrogen ion and bicarbonate has not been measured directly.

The equilibrium constant for reaction 4 is given by

$$K = \frac{C\alpha^2}{(1 - \alpha)50} \quad (5)$$

in dilute solution where the concentration of the solvent remains constant and $C$ is the total boron trifluoride concentration. The degree of association of the boron trifluoride, $\alpha$, is given by

$$\alpha = \Lambda/\Lambda' \quad (6)$$

where $\Lambda$ is the measured equivalent conductance and $\Lambda'$ is the equivalent conductance at the existing

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[1] Abstracted in part from the Ph.D. thesis of Fred E. Luborsky, Illinois Institute of Technology, June, 1952.

[2] Presented before the Division of Physical and Inorganic Chemistry at the 125th Meeting of the American Chemical Society, Kansas City, April, 1954.

[3] Fulbright Research Scholar in 1953 at the Royal Veterinary and Agricultural College, Copenhagen, Denmark.

ion concentration if complete dissociation exists. Using these relations the over-all equilibrium for postulated interaction of boron trifluoride in hydrofluoric acid may be calculated.

## Experimental

The purification and handling of the boron trifluoride and hydrofluoric acid have already been described.[4] The quantity of boron trifluoride introduced into the conductance cell containing the hydrofluoric acid was calculated from the decrease in pressure in the storage systems. Two systems were used to deliver the gas. For pressures up to two atmospheres absolute pressure, an all-glass system with a mercury manometer was used, but for higher pressures a steel tank was used with a 0–1000 lb. Bourdon tube gage. The gage could be read to ±0.5 p.s.i. The volumes of these two systems were measured by first evacuating to less than $10^{-2}$ mm. and then filling with air up to atmospheric pressure from a gas buret. The volumes were thus calibrated to ±0.01 ml. The density of boron trifluoride at atmospheric pressure and below is known from the precise measurements of Rumold[5] at 0° and from the less precise data of Fisher[6] at 20°. No measurements above one atmosphere were found in the literature. Our measurements were obtained by collecting increments of gas from the high pressure system in a large gas buret at atmospheric pressure. From the known volume and temperature of the gas collected, the moles of gas delivered from the tank between the two pressures could be calculated from the data of Rumold and of Fisher. The results, with an estimated precision of measurement of 0.5%, are shown in Fig. 1 and compared to the ideal line. Two independent series of measurements were made at 19.2° from 800 to 15 p.s.i. absolute, in intervals of about 40 p.s.i. The high pressure tank was immersed in a Dewar flask filled with water to maintain constant temperature during measurements. An 800-ml. gas buret was used, with mineral oil saturated with boron trifluoride as a sealing liquid and Drierite protecting the leveling bulb from moisture. The Bourdon gages were calibrated to ±0.5 p.s.i. with a dead weight tester. The curve can be represented by the equation

$$PV^2 = 344V - 30.9 \qquad (7)$$

with the calculated values of the pressure agreeing with the experimental values to 1%, where $P$ is in atmospheres and $V$ in liters per mole.

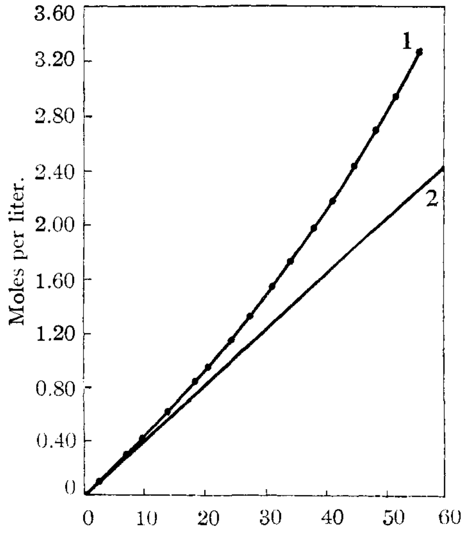

Fig. 1.—The compressibility of $BF_3$ at 19°: 1, observed; 2, ideal.

The actual concentration of boron trifluoride in the hydrofluoric acid was the difference between the total gas added and the gas remaining in the vapor phase above the solution. The latter quantity was calculated from the measured volumes of the cell and of the liquid and by assuming Dalton's law. The amount of boron trifluoride in the gas phase was never greater than 15% of the total so that even a large error in its determination resulted in a small error of the calculation of the quantity of gas in solution.

At low pressures the total pressure of the system was found to be a linear function of the molality of boron trifluoride in the solution, namely

$$P = 7.17m + 1.0 \text{ atmospheres} \qquad (8)$$

as shown in Fig. 2. This is to be expected even though there is chemical interaction between the boron trifluoride and hydrofluoric acid since, as will be shown later, the magnitude of the interaction is so small. The deviation from linearity at higher pressures can be attributed to the compressibility of the gas or to deviations from Dalton's law. The results of McCaulay and Lien[7] are also presented in Fig. 2.

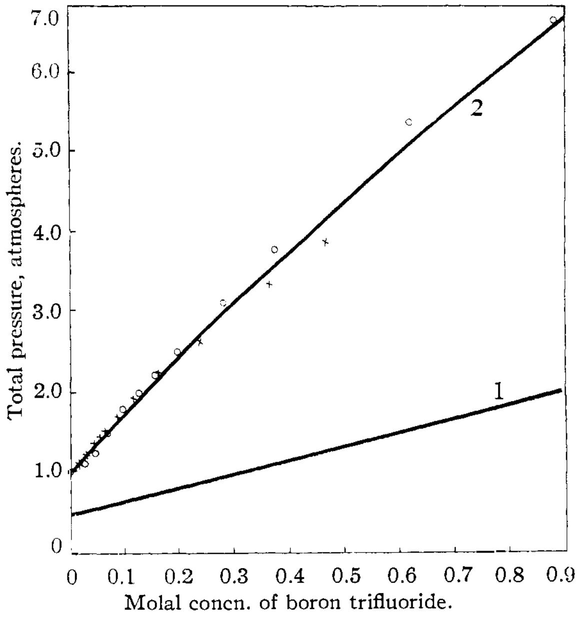

Fig. 2.—Solubility of $BF_3$ in HF: 1, McCaulay and Lien at 0°; this investigation at 19°.

The conductance cell and electrical measurements also have been described previously.[4] The equivalent conductance curves are shown in Fig. 3 for two independent runs. The difference in the two curves is caused by a difference of a factor of 2 in the specific conductance of the solvent. If the conductance of the solvent were attributable to water, it is estimated from the data of Fredenhagen and Cadenbach[8] that the water concentrations would be 0.00066 and 0.0013 $m$, respectively. As water would be a strong base in this system, it should have a large effect even at these low concentrations.

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(4) M. Kilpatrick and F. E. Luborsky, THIS JOURNAL, **75**, 577 (1953).

(5) C. F. Rumold, Ph.D. Thesis, Western Reserve University, 1931.

(6) W. Fisher, *Z. anorg. allgem. Chem.*, **213**, 106 (1933).

(7) D. A. McCaulay and A. R. Lien, THIS JOURNAL, **73**, 2013 (1951).

(8) K. Fredenhagen and G. Cadenbach, *Z. physik. Chem.*, **146**, 245 (1930).

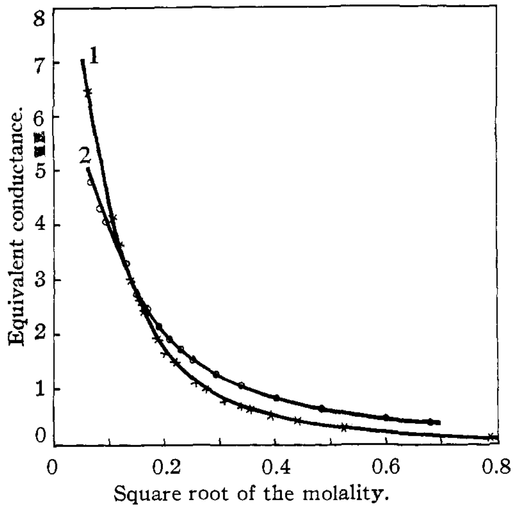

Fig. 3.—Equivalent conductance of $BF_3$ in HF, specific conductance of solvent: 1, $1.9 \times 10^{-4}$ ohm$^{-1}$ cm.$^{-1}$; 2, $3.8 \times 10^{-4}$ ohm$^{-1}$ cm.$^{-1}$.

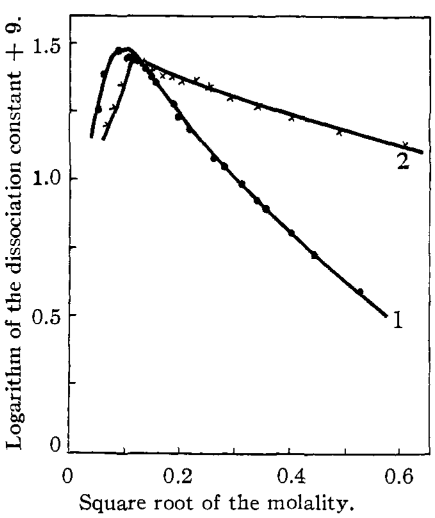

Fig. 4.—The interaction of $BF_3$ with HF, specific conductance of solvent: 1, $1.9 \times 10^{-4}$ ohm$^{-1}$ cm.$^{-1}$; 2, $3.8 \times 10^{-4}$ ohm$^{-1}$ cm.$^{-1}$.

In order to calculate the equilibrium constant for equation 4, we need to know the equivalent conductance, $\Lambda'$, of the completely dissociated $H_2F^+{\cdot}BF_4^-$ at various concentrations. As no strong proton acid is known in anhydrous hydrofluoric acid, the ionic conductance of the $H_2F^+$ is not available. In order to make the calculation, the assumption is made that the ionic conductance of $H_2F^+$ is the same as that of the $K^+$ ion. The equivalent conductance of $KBF_4$ has been evaluated.[9] These values were used to calculate $\alpha$ and $\Lambda'$ by successive approximations using $\Lambda' = \Lambda^0$ as a first approximation. The results of these calculations are shown in Fig. 4. These results should be considered as approximate and the points before the maximum should be attributed to impurities in the solvent.

We have now available the data to make an approximate calculation of the autoprotolysis constant and the ion product constant of hydrofluoric acid from the equilibrium constant of equations 3 and 4. The equilibrium constant for equation 2 is given by

$$K_1 = \frac{[H_2F^+][F^-]}{[HF]} = K_3K_4 \qquad (9)$$

The constant for (4) is $1.4 \times 10^{-9}$ at the highest ion concentration measured, 0.00025 *m*, and the constant for (3) is $2.7 \times 10^{-3}$ at the lowest concentration measured,[9] namely, 0.045 *m*. In extrapolating to some intermediate concentration both equilibrium constants decrease. As an approximation $K_1 < 4 \times 10^{-12}$ and $[H_2F^+]\ [F^-] < 2 \times 10^{-10}$. This value of the ion product is much larger than the ion product of water, $10^{-14}$, but smaller than that for 100% sulfuric acid, $10^{-4}$.[10]

The specific conductance of hydrofluoric acid can be calculated from the ion product of $2 \times 10^{-10}$ if we again assume the mobility of the $K^+$ ion is the same as that of $H_2F^+$. Then the conductance curve for potassium fluoride[6] can be used to represent the conductance of the completely dissociated species. On this basis the specific conductance corresponding to an ion product of $2 \times 10^{-10}$ calculates to be less than $0.7 \times 10^{-5}$ ohm$^{-1}$cm.$^{-1}$ as compared with our experimental value of $1 \times 10^{-4}$ ohm$^{-1}$ cm.$^{-1}$ at 20°. In fact Fredenhagen and Cadenbach[11] have reported a value of $0.14 \times 10^{-4}$ ohm$^{-1}$ cm.$^{-1}$ at $-15°$ in cells of noble metals, which is about a factor of 5 lower than our value at the same temperature. Our latest results in fluorothene cells also show lower specific conductances for hydrofluoric acid.

Whether the interaction of $BF_3$ with hydrofluoric acid is through the intermediate $HBF_4$ or by the direct interaction of $BF_3$ with the fluoride ion according to equation 3 is an interesting question. One general definition of acids is that an acid is a substance which increases the concentration of the solvent cation. Such a definition is also applicable to equilibria of interhalogens in the solvent hydrogen fluoride.

$$IF_5 + HF \rightleftharpoons IF_4^+ + HF_2^- \qquad (10)$$

and to the reaction

$$F^- + SbF_5 \rightleftharpoons SbF_6^- \qquad (11)$$

where the addition of $SbF_5$ displaces reaction 10 to the right. Similar reactions take place in the displacement of self-ionization of the interhalogens themselves.[12] In all cases the displacement can be explained in terms of the reaction represented by equation 3. We propose the term *co-acid* for these fluoride ion acceptors and would point out that hydroxyl ion acceptors such as $CO_2$, $SO_2$, etc., are co-acids in the same sense in aqueous solution

$$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$$
$$OH^- + CO_2 \rightleftharpoons HCO_3^-$$

These mechanisms are not in disagreement with the

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(9) M. Kilpatrick and F. E. Luborsky, THIS JOURNAL, **76**, 5863 (1954).

(10) R. J. Gillespie and S. Wasif, *J. Chem. Soc.*, 964 (1953).

(11) K. Fredenhagen and G. Cadenbach, *Z. anorg. allgem. Chem.*, **178**, 289 (1929).

(12) A. A. Woolf and H. J. Emeléus, *J. Chem. Soc.*, 2865 (1949).

results of Faurholt[13] and the calculations of Olson and Youle.[14]

It would be interesting to determine the equilibrium constant of reaction 3 where $SbF_5$ and $AsF_5$ replace $BF_3$, in reactions involving fluoride salts and interhalogens such as those represented by equations 10 and 11.

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(13) C. Faurholt, *J. chim. phys.*, **22**, 1 (1925).

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[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

# Polarography of Iron Oxalates, Malonates and Succinates[1a,b]

BY WARD B. SCHAAP,[1c] H. A. LAITINEN AND J. C. BAILAR, JR.

RECEIVED JUNE 7, 1954

The polarographic method was employed to study the iron(II) and iron(III) complexes that exist in oxalate, malonate and succinate solutions. With oxalate solutions, evidence for the existence of $Fe(C_2O_4)_2^{-2}$, $Fe(C_2O_4)_3^{-4}$ and $Fe(C_2O_4)_3^{-3}$ is presented together with dissociation constants evaluated from polarographic and solubility data. With malonate solutions, $Fe(C_3H_2O_4)_2^{-2}$ and $Fe(C_3H_2O_4)_3^{-3}$ are identified and their dissociation constants calculated. The studies with succinate solutions were inconclusive since most of the waves could not be shown to be reversible.

Previous polarographic investigation of the complexes of iron with anions of this homologous series of dicarboxylic acids is limited to the oxalato complexes. Stackelberg and Freyhold[2] report that the polarographic half-wave potentials remain constant at $-0.24$ volt (*vs.* S.C.E.) in oxalate solutions ranging from 0.01 to 1.0 *M* concentration, concluding that the complexes present in this concentration range are the trioxalatoferrate(III) ion and its reduction product, the trioxalatoferrate(II) ion. Lingane[3] found, however, that the half-wave potentials remain constant at about $-0.242$ volt only when the oxalate ion concentration is greater than 0.15 *M*. At lower oxalate concentrations the data indicate the reduction product to be the dioxalatoferrate(II) ion. Using the solubility data of Schaper,[4] Lingane recalculated the dissociation constant of the trioxalatoferrate(II) complex to be $6.1 \times 10^{-7}$, and with the ratios between the dissociation constants of the iron(III) and iron(II) complexes obtained polarographically, calculated the dissociation constants of the other two complexes to be $8 \times 10^{-6}$ and $6 \times 10^{-20}$ for the dioxalatoferrate(II) and the trioxalatoferrate(III) ions, respectively. Toropova[5] reports dissociation constants which vary considerably from those of Lingane, *i.e.*, for the dioxalatoferrate(II) ion, $K_d = 2.7 \times 10^{-10}$ and for the trioxalatoferrate(III) complex, $K_d = 1.2 \times 10^{-24}$. Lingane[6] also studied the analytical aspects of the iron–oxalate system, finding that well-developed, reversible waves are obtained with acidic and neutral solutions, while in basic solutions the waves disappear due to precipitation of the iron(III) hydroxide.

The present paper reports the results of a reinvestigation of the polarography of iron in oxalate solutions together with results of a systematic study with malonate solutions and an attempted study with succinate solutions. These dicarboxylate anions constitute a series of symmetrical chelating agents with gradually increasing ring size and of highly polar character.

## Experimental

**Apparatus.**—All polarograms were made with a Sargent Model XXI Recording Polarograph. Potentials were measured against the saturated calomel electrode (S.C.E.) with a portable Rubicon potentiometer. The *p*H values of solutions were measured with a glass electrode and a Beckman Model G *p*H meter.

Polarograms of oxalate and dilute malonate solutions were made using an H-type cell with a temporary agar plug (3% agar and 0.5 *M* $NaClO_4$). The resistance of such cells together with that of the dropping mercury electrode was found to be about 500 ohms. The more concentrated solutions used in the malonate and succinate studies were found to shrink the agar plug rapidly, so for these solutions an H-type cell with a 20-mm. fine sintered glass plug and a resistance of about 700 ohms was used. All polarograms were run at 25.0 ± 0.2°. The capillary constant ($m^{2/3}t^{1/6}$) for the electrode used was 2.25 at $-0.4$ v., the potential at which most diffusion currents were measured. Purified nitrogen was used to remove dissolved oxygen from cell solutions.

**Materials.**—A standard iron(III) perchlorate solution was prepared by dissolving crystalline iron(III) perchlorate-6-hydrate in distilled water and standardized by titrating a reduced sample with a standard cerate solution. The potassium oxalate solution was prepared from the reagent grade salt and standardized by titration with standard cerate solution. Potassium malonate and potassium succinate were not available and were prepared from the acids. The technical grade acids were washed with ether and then crystallized twice from water. The recrystallized acid was dissolved in water, excess potassium hydroxide added and the solution heated and filtered to remove heavy metal hydroxides. The salt was crystallized from the filtrate by evaporation and cooling and then recrystallized from distilled water. The purified salts were dried to constant weight in a vacuum desiccator over $P_2O_5$. Carbon and hydrogen analyses were made to verify the composition of the anhydrous salts. Weighed amounts of these salts were used to prepare the standard malonate and succinate solutions.

In the more dilute solutions, reagent grade sodium perchlorate was added to bring the ionic strength up to a minimum value of 0.5. No maximum suppressors were required or used throughout this work.

**Procedure.**—All solutions were made up to contain $1.00 \times 10^{-3}$ *M* iron(III) perchlorate and varying amounts of the dicarboxylate salts. The actual concentration of the dival-

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(1) (a) Presented by Ward B. Schaap in partial fulfillment of the requirements for the degree of Doctor of Philosophy to the Graduate College of the University of Illinois, 1950. (b) Presented at a symposium on "Equilibrium and Rate Behavior of Complex Ions," University of Chicago, February 21–23, 1951. (c) Graham, Crowley and Associates and Burgess Battery Company Fellow, 1948–1949; Atomic Energy Commission Predoctoral Fellow, 1949–1950. Present address, Department of Chemistry, Indiana University, Bloomington, Indiana.

(2) M. v. Stackelberg and H. v. Freyhold, *Z. Elektrochem.*, **46**, 120 (1940).

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(5) V. Toropova, *J. Gen. Chem.* (*U.S.S.R.*), **11**, 1211 (1941).

(6) J. J. Lingane, THIS JOURNAL, **68**, 2448 (1946).