strongly heating the tube leading from the reaction vessel. The resulting flame was yellow-brown in color and could be held in place by a constriction in the tube. This flame is undoubtedly caused by the oxidation of ammonia by nitric acid vapors, together with the decomposition of N_2O. The brown color of NO_2 was evident in the products. In one experiment, the flame flashed back through the constriction to the surface of the NH_4NO_3 in the reaction vessel. The evolved gases burned quietly at the surface of the melt until the nitrate was consumed.

B. **Reaction Rate.**—The reaction rate was measured by preheating a 500-ml. silvered Pyrex dewar flask to about 275°, by means of an inserted electric heater. When the required temperature had been attained, the heater was removed, 300 g. of molten NH_4NO_3 at approximately the same temperature was added, and the flask was loosely closed with an insulated glass cover through which a mercury thermometer was inserted into the melt. The entire assembly was placed on a platform balance and weighed at suitable intervals.

Over an interval of about 3 minutes, during which time 110 g. of NH_4NO_3 was consumed, the temperature rose to 290° (corrected for stem exposure) and leveled off. This temperature is somewhat lower than the 292° reported in Table II because of heat loss from the dewar flask. The temperature remained steady for about ten minutes, at the end of which time only about 50 g. of nitrate remained. Dense clouds of white fume were evolved during the reaction, as a result of dissociation and recombination of NH_4NO_3. The loss in weight of the flask during the constant temperature reaction is given in Table III, together with the calculated values of the over-all rate constant, which includes the NH_4NO_3 lost by vaporization.

The authors take pleasure in acknowledging the advice and coöperation of Dr. Alfred G. Emslie and Dr. William E. Gordon.

This work was performed, in part, under the auspices of the United States Coast Guard and the Advisory Committee on Hazards of Ammonium Nitrate Transportation of the National Research Council. Permission to publish this article has been granted by the United States Coast Guard, but neither of the sponsoring agencies necessarily approves the technical opinions or conclusions therein expressed.

CAMBRIDGE, MASS.

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

The Dissociation of Fluoborate Ion in Anhydrous Hydrofluoric Acid[1,2]

BY MARTIN KILPATRICK[3] AND FRED E. LUBORSKY

RECEIVED JUNE 7, 1954

In a previous paper, the equilibrium constants for the reaction Ar + HF $\rightleftarrows$ $ArH^+ + F^-$ were reported for the methylbenzenes and shown to vary from 10^{-8} to 10^{-2}. When sufficient boron trifluoride was introduced into the system, it was shown that essentially all of the aromatic was converted to the aronium ion and it was assumed that the addition of BF_3 established a second equilibrium $F^- + BF_3 \rightleftarrows BF_4^-$. Further support for the existence of this equilibrium and the calculation of this equilibrium constant are the subjects of the present paper. This constant has been evaluated from conductance studies on potassium fluoride and potassium fluoborate, and from the change in conductance of potassium fluoride on addition of boron trifluoride. Both methods give a value approximating 2×10^2 at 20°, or 5×10^{-3} for the dissociation of the fluoborate ion.

In an earlier paper[4] the equilibrium constants were reported for the reaction

$$Ar + HF \rightleftarrows ArH^+ + F^- \qquad (1)$$

where Ar represented benzene or a methylbenzene. It was also shown that reaction 1 could be displaced to the right by the addition of a fluoride acceptor such as boron trifluoride

$$F^- + BF_3 \rightleftarrows BF_4^- \qquad (2)$$

The existence of such an equilibrium is shown by means of conductance studies on potassium fluoborate and potassium fluoride in the solvent anhydrous hydrofluoric acid, and conductance and vapor pressure studies on the addition of boron trifluoride to potassium fluoride.

Figure 1 gives the specific conductance of potassium fluoride on addition of boron trifluoride and the curves are analogous to those reported in the previous paper[4] for the addition of boron trifluoride to solutions of certain of the methylbenzenes, namely, mesitylene, isodurene, pentamethylbenzene and hexamethylbenzene. The interpretation of the decrease in specific conductance on addition of boron trifluoride is that the fluoride ion is replaced by the less mobile fluoborate ion. This is substantiated by the curves of the total vapor pressure of these same solutions as shown in Fig. 2. The curves indicate almost complete reaction of

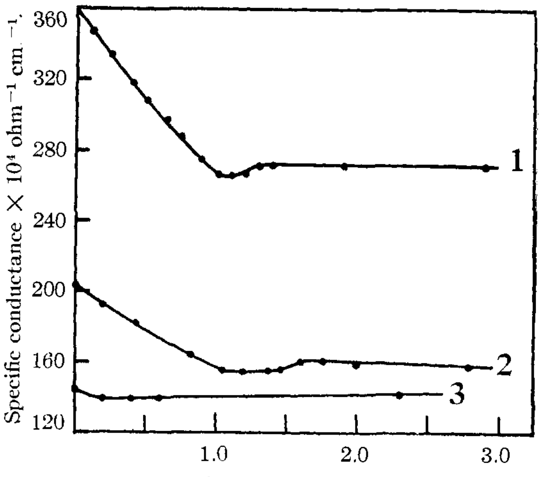

Fig. 1.—The conductance of salts in anhydrous hydrofluoric acid on the addition of boron trifluoride: 1, 0.104 *m* KF; 2, 0.0512 *m* KF; 3, 0.0447 *m* KBF_4.

---

[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.

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

the boron trifluoride up to a 1:1 mole ratio, followed by a region in which Henry's law is applicable. Curve 3 of Fig. 2 for potassium fluoborate shows no deviation from Henry's law, but the more sensitive conductance method (Fig. 1) shows an initial dip indicating that the fluoborate ion is somewhat dissociated into fluoride ion and boron trifluoride before boron trifluoride is added. The increase in the specific conductance in curves 1 and 2 before leveling off is due to the increase in the concentration of solvated proton as the boron trifluoride reacts with fluoride from the autoprotolysis of the solvent itself.

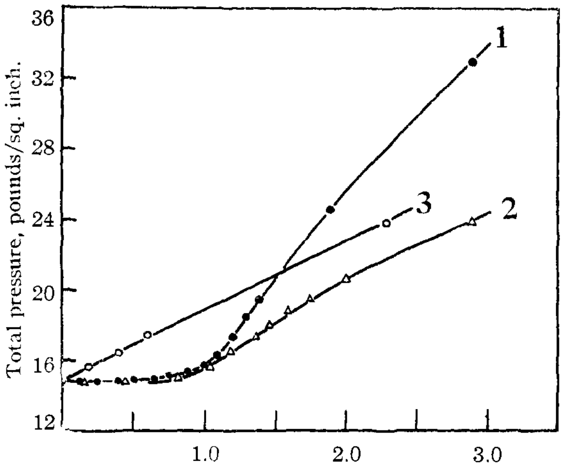

Fig. 2.—The vapor pressure over solutions of salts in anhydrous hydrofluoric acid on the addition of boron trifluoride: 1, 0.104 *m* KF; 2, 0.0512 *m* KF; 3, 0.0447 *m* KBF_4.

We will now proceed to show how the equilibrium constant for reaction 2 can be calculated from the conductance data. In the previous paper it was shown that the equivalent conductance of the methylbenzenes in hydrofluoric acid in the presence of excess boron trifluoride can be reasonably well represented by one curve (Fig. 6 of ref. 5). This was taken to be the equivalent conductance of the salt $ArH^+{\cdot}BF_4^-$. The curve for hexamethylbenzene in hydrofluoric acid alone indicated that reaction 1 was far enough to the right in dilute solution to permit a calculation of the equivalent conductance of the strong (completely dissociated) electrolyte $ArH^+{\cdot}F^-$. The difference in conductance between the two curves gives the difference in conductance between the fluoride and fluoborate ions. Subtracting this value from the measured equivalent conductance of potassium fluoride which is assumed to be completely dissociated in the high dielectric solvent hydrogen fluoride gives the equivalent conductance of the strong electrolyte $K^+BF_4^-$ where the fluoborate ion is not dissociated to fluoride and boron trifluoride. This calculated curve is given as curve 2 of Fig. 3, while curve 3 gives the experimental curve for potassium fluoride and curve 1 that for potassium fluoborate. The difference between curves 1 and 2 is due to the equilibrium

$$BF_4^- \rightleftarrows F^- + BF_3 \qquad (2a)$$

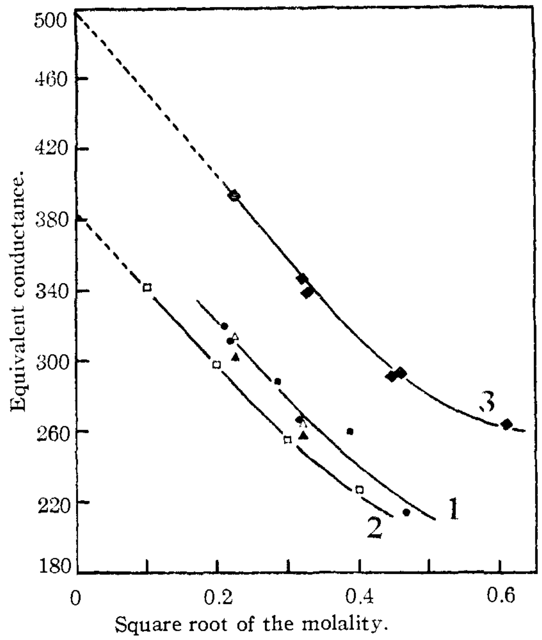

Fig. 3.—Equivalent conductance of salts in hydrofluoric acid: 1, ●, KBF_4 observed; ▲, KBF_4 observed at the minimum in curve of KF on addition of BF_3; △, KBF_4 observed for excess BF_3 added to KF; 2, KBF_4 calculated for complete dissociation into $K^+ + BF_4^-$; 3, KF observed.

and the equilibrium constant

$$K = [F^-][BF_3]/[BF_4^-] \qquad (3)$$

can be calculated in the usual way in terms of the degree of dissociation, α, where α is exactly expressed by

$$\alpha = \frac{\Lambda - \Lambda_{KBF_4}}{\Lambda_{KF} - \Lambda_{KBF_4}}$$

where Λ_{KBF_4} and Λ_{KF} are the equivalent conductance of the completely dissociated salts at the ion concentration of the solution. Since the conductance differences are small, great accuracy cannot be expected. The values of Λ are taken from the smooth curve 1 of Fig. 3. The equilibrium constants calculated in this way are tabulated in Table I.

TABLE I

THE EQUILIBRIUM CONSTANT FOR $BF_4^- \rightarrow F^- + BF_3$ FROM MEASUREMENTS ON POTASSIUM FLUOBORATE AT 20°

KBF_4, *M*	Equiv. conductance	Equilibrium constant	KBF_4, *M*	Equiv. conductance	Equilibrium constant
0.0447	315.5	0.0027	0.1005	271	0.0060
.0489	312	.0029	.1517	244.5	.0083
.0826	283	.0051	.217	220.5	.0073

The equilibrium constant for reaction 2a can also be calculated from the measurements on potassium fluoride in the presence of boron trifluoride. In this case

$$K = \frac{1 - \beta}{\beta}\left(C_{BF_3} - \beta C_{F^-}\right)$$

for $C_{BF_3} < C_{F^-}$ and where β is expressed by

$$\beta = \frac{\Lambda_{KF} - \Lambda}{\Lambda_{KF} - \Lambda_{KBF_4}}$$

The results are tabulated in Table II.

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

[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 2×10^{-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

$$BF_3 + HF \rightleftharpoons (HBF_4) + HF \rightleftharpoons H_2F^+ + BF_4^- \quad (1)$$

dissolved

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

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

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

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

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

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, α, is given by

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

where Λ is the measured equivalent conductance and Λ' is the equivalent conductance at the existing

---

(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.