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

The Base Strengths of Aromatic Hydrocarbons Relative to Hydrofluoric Acid in Anhydrous Hydrofluoric Acid as the Solvent[1]

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Apparatus is described to prepare hydrofluoric acid of high purity. The conductances of potassium fluoride and of the methyl substituted benzenes, including benzene, have been measured in this acid at several concentrations at 20.0°. The conductances of these same solutions were also measured in the presence of boron trifluoride up to a pressure of 100 lb. per sq. in. It has been shown that the principal equilibrium existing in solutions of methylbenzenes in hydrofluoric acid is $Ar + HF \rightleftarrows ArH^+ + F^-$. The stoichiometric equilibrium constant for this reaction calculated from the conductance data ranged from 10^{-8} for benzene to 10^{-2} for hexamethylbenzene. This order of the basic strengths of the methylbenzenes relative to hydrofluoric acid is substantially in agreement with the results of previous workers arrived at by other techniques. Our results indicate that the boron trifluoride reacts only with the fluoride ion. Isomerization of the tetramethylbenzenes, but not of the xylenes or trimethylbenzenes in anhydrous hydrofluoric acid is reported, and the role of hydrofluoric acid–boron trifluoride mixtures as catalysts in organic reactions is discussed briefly. Our results indicate that the ArH^+ cation can be quite stable and is an important intermediate in these systems.

There is now considerable evidence that aromatic nuclei possess basic properties. The origin of this basicity however is still open to question. It has been attributed[2] to π-electron bonding or to carbonium ion formation.[3,4] Whatever its origin, the relative basicity of these compounds has been measured by a variety of techniques as indicated in Table I. Measurements of this basicity in hydrofluoric acid are of interest both because of the lack of knowledge as to the mechanism of isomerizations in this medium and also because of the sparseness of conductance data in this highly acidic solvent. The high dielectric constant and low viscosity of HF makes it a convenient solvent for conductance work. McCaulay[4] has presented data on the distribution of various aromatics between *n*-heptane and HF, and on batch extraction experiments in which methylbenzene mixtures were treated with hydrogen fluoride and controlled amounts of boron trifluoride. They also reported vapor pressure data on the systems aromatic–boron trifluoride–hydrogen fluoride. From this they set up a scale of base strengths for the methylbenzenes relative to hydrofluoric acid in the presence of boron trifluoride.

TABLE I

THE RELATIVE BASICITY OF METHYLBENZENES AS DETERMINED BY VARIOUS METHODS[a]

Reference acid →	HF	$HF–BF_3$	Ag^+		HCl	I_2
Methylbenzene	Relative basicity at 0.1 molal	Relative basicity[b]	K_{Ar,Ag^+}[c]	K_{ArAg^+,Ag^+}[c]	Henry's law constant,[d] mm. (in toluene)	Light absorption[e] λ_{max}, mμ
Benzene	0.09		2.41	0.212	308	297
Toluene	0.63	0.01	2.95	.214	299	306
p-Xylene	1.0	1.00	2.63	.331	294	315
o-Xylene	1.1	2	2.89	.315	286	319
m-Xylene	26	20	3.03	.320	278	
Pseudocumene (1,2,4-)	63	40			272	
Hemimellitene (1,2,3-)	69	*ca.* 40			265	
Durene (1,2,4,5-)	140	120				
Prehnitene (1,2,3,4-)	400	170				
Mesitylene (1,3,5-)	13000	2800	1.80		254	333
Isodurene (1,2,3,5-)	16000	6500				
Pentamethylbenzene	29000	8700				
Hexamethylbenzene	97000	89000				

[a] See also M. Tamres, THIS JOURNAL, 74, 3375 (1952). [b] As computed from the data of McCaulay and Lien,[4] by Brown and Brady.[19] [c] L. J. Andrews and R. M. Keefer, THIS JOURNAL, 71, 3644 (1949); 72, 3113 (1950). [d] H. C. Brown and J. D. Brady, *ibid.*, 71, 2573 (1949). [e] H. A. Benesi and J. H. Hildebrand, *ibid.*, 71, 2703 (1949).

Experimental

The Preparation and Handling of the Hydrofluoric Acid.—Since hydrofluoric acid has a high affinity for water, it was quite difficult to remove the last traces of moisture from the acid. Corrosion of the equipment was particularly bad because fluorides of the metals were produced and, in addition, water was produced from the oxide films or occluded oxides in the metal. Water must be excluded not only because it is a strong electrolyte in the solvent hydrofluoric acid but also because it is a strong base and will therefore interfere with acid–base equilibrium being studied, *i.e.*

$$H_2O + HF \rightleftarrows H_3O^+ + F^- \qquad (1)$$

With the above points in mind, the system shown schematically in Fig. 1 was evolved. This apparatus was used to prepare the hydrofluoric acid, fractionally distil the acid, and measure the volume delivered into the conductance cell. The materials used in its construction were principally monel and Kel-F (monochlorotrifluoroethylene polymer). The metal-to-metal joints were either silver-soldered or joined by Aminco high pressure couplings. The plastic-to-metal joints were all mechanical press fits. The system was vacuum tight and would withstand at least two atmospheres absolute pressure.

The hydrofluoric acid was prepared by the thermal decomposition of technical grade potassium acid fluoride ac-

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

[2] M. J. Dewar, *J. Chem. Soc.*, 406 (1946).

[3] H. C. Brown and H. W. Pearsall, THIS JOURNAL, 74, 191 (1952).

[4] D. A. McCaulay and A. P. Lien, *ibid.*, 73, 2013 (1951).

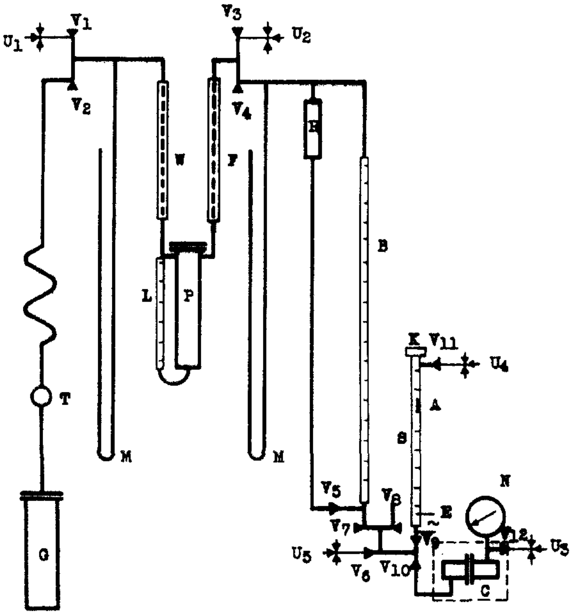

Fig. 1.—Schematic diagram of the hydrofluoric acid system.

A	Iron bar encased in Kel-F
B	Kel-F buret, 30 ml. calibrated to ±0.02 ml.
C	Conductance cell in a constant temperature chamber
E	Electrodes
F	Fractionating column
G	Silver hydrofluoric acid generator, holds about 2 pounds KHF_2
K	Removable cap
L	Kel-F liquid level gage
M	Kel-F mercury filled manometer
N	Bourdon tube pressure gage
P	Monel storage tank
R	Teflon receiving tank
S	Kel-F mixing buret 10 ml. calibrated to ±0.02 ml.
T	Trap
U_1 to U_5	Utility inlets for high vacuum, purified nitrogen, and aspirator
V_1 to V_{11}	Monel valves, Teflon packed
W	Cold water jacket

cording to the procedure of Fredenhagen and Cadenbach.[5] About two pounds of this salt in the silver vessel G, was dried overnight under vacuum and then for about one hour at 200° before use. The acid collected in the first receiver P had a specific conductance of 31 × 10^{-4} ohm^{-1} cm.$^{-1}$ at 5°. The acid was then distilled as needed in the closed system through tower F, which removed any salt or water. This tower was a half-meter monel tube, packed loosely with Teflon turnings and surrounded by a jacket maintained at 20° by water from a constant temperature bath. The pressure, as read on manometers M_1 and M_2, was adjusted during the distillation to the boiling point of the acid by means of the valves at V_4. These manometers were mercury-filled U-tubes with Kel-F tubing on the system side and glass tubing on the atmosphere side. This final distillation gave acid with a minimum specific conductance of 0.98 × 10^{-4} ohm^{-1} cm.$^{-1}$ at 20.0°. This value corresponded to 0.5 × 10^{-4} ohm^{-1} cm.$^{-1}$ at −15° as compared to the minimum value of 0.14 × 10^{-4} ohm^{-1} cm.$^{-1}$ at −15° reported by Fredenhagen and Cadenbach.[5] However their apparatus was constructed entirely of noble metals. The extrapolation from 20 to −15° was made on the basis of some preliminary temperature coefficient measurements. No attempt was made to really flush out the system to try to obtain acid of minimum conductance. The acid actually used had a specific conductance of from 1 to 4 × 10^{-4} ohm^{-1} cm.$^{-1}$ at 20°. On the basis that water is the only impurity present, 2 × 10^{-4} ohm^{-1} cm.$^{-1}$ would correspond to less than 0.0005 molal concentration of water.[6]

The Conductance Cell.—The manifold system and the conductance cell assembly were built to withstand at least 600 lb. per sq. in. Aminco high pressure needle valves packed with Teflon were used here, and all tubing and other parts were also monel. It was soon found that in the presence of boron trifluoride, the conductance of the solutions changed rapidly, due to increased corrosion. For this reason all of the valves, tubing and other exposed parts in the manifold system and in the cell were given a heavy plating of silver and then platinum. Standard plating solutions[7] were used and found to be satisfactory.

The conductance cell is shown in Fig. 2. It contained two bright platinum electrodes P, of about 1 sq. cm. area, made by plating directly on monel tapered plugs. The electrical path was insulated by the Teflon tube T, tapered to fit the electrodes at the end and joined by flanges at the center. The tubing to the pressure gage and valve was lined with Kel-F tubing. These plastic parts were snugly fitted into the monel body. A bourdon tube pressure gage with a range of 0 to 1000 lb. attached to the cell was protected from the acid by means of a platinum-plated monel diaphragm. The gage could be read to ±0.5 lb. The cell itself was maintained at 20.0 ± 0.1° by circulating water through copper coils wound around the cell.

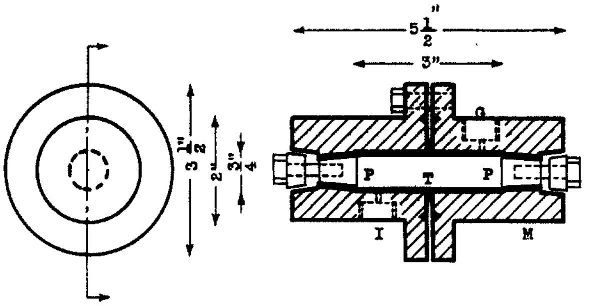

Fig. 2.—High pressure conductance cell.

G	To the gage
I	Inlet and outlet opening
M	Monel body
P	Bright platinum electrodes
T	Teflon tube

The resistance measurements were made on a General Radio type 650-A bridge equipped with decade capacitors for balancing out the cell and lead capacitance. A resistance capacitance oscillator with fixed frequencies of 521, 729, 889, 1580 and 2340 cycles per sec. was used. Since no polarization was found in either the aqueous solutions of KCl or in any of the HF solutions all of the measurements were made at 889 cycles per sec. The signal from this oscillator, applied across the bridge, was amplified and detected by an electronic eye tube using standard circuits.[8,9] The null point indicated by a maximum opening of the eye was sufficiently sensitive to set the bridge dial to the same reading each time. Resistances could be read to three significant figures in all ranges.

The cell constant was determined by using 1.00, 0.100, 0.0100, 0.00333 and 0.00100 molar potassium chloride solutions. The cell constant at all concentrations except 0.00100 molar, was 4.90 ± 0.04 cm.$^{-1}$. At 0.00100 molar, the cell constant was 4.74 cm.$^{-1}$. The specific conductance of the water used in these solutions was 2.3 × 10^{-6} ohm^{-1} cm.$^{-1}$.

The Preparation of Solutions.—Solutions of the compounds in hydrofluoric acid were made up by introducing a known amount of solid or liquid into the empty mixing buret S, through the cap K, while maintaining at all times a flow of nitrogen from V_{11}. Hygroscopic solids, such as potassium fluoride, were redried by evacuation in this buret. A known volume of acid was then introduced and the solution mixed by moving the Kel-F encased iron bar A, with a magnet. This solution was then introduced into the cell C, and additional pure acid added to fill the conductance chamber. Final mixing was accomplished by returning the solution from the cell to the small buret, mixing, and then returning it to the cell again. Only one or two such mixing operations were required. Dilutions of the cell contents were made by withdrawing a measured volume of the solution from the cell into the small buret and replacing it

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

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

[7] "Plating and Finishing Guidebook," The Metal Industry Publishing Co., New York, N. Y., 1940, pp. 50, 57.

[8] G. M. Evans, *J. Chem. Education*, **15**, 389 (1938).

[9] F. Hovorka and E. Mendenhall, *ibid.*, **16**, 239 (1939).

TABLE II

PHYSICAL CONSTANTS OF THE PURIFIED HYDROCARBONS

Hydrocarbon	B.p. at 760 mm. in °C. Detd.	B.p. at 760 mm. in °C. Lit.[a]	Refractive index $n^{20}D$ Detd.	Refractive index $n^{20}D$ Lit.	Original material Source	Original material Probable impurities
n-Pentane	36.1	36.1	1.3576	1.3577	Phillips	Isopentane
Benzene	80.2	80.2	1.5008	1.5009	Baker & Adamson	
Cyclohexane	80.8	80.8	1.4259	1.4265	Phillips	Dimethylpentanes
Methylcyclohexane	101.1	100.3	1.4232	1.4231	Phillips	Ethylcyclopentane
Toluene	110.8	110.6	1.4966	1.4962	Baker & Adamson	
p-Xylene	138.7	138.4	1.4954	1.4958	Matheson	*m*-Xylene
m-Xylene	139.0	139.1	1.4971	1.4972	Matheson	*p*-Xylene
o-Xylene	144.1	144.2	1.5043	1.5052	Matheson	
Mesitylene	164.7	164.7	1.4979	[b]	Matheson	
Pseudocumene	168.9	169.3	1.5002	1.5049	McCaulay	[c]
Hemimellitene		176.5		1.5134	Bureau of Standards	
Isodurene	197.6	197.2	1.5132	1.5195	McCaulay	[e]
Prehnitene	204.6	205.0	1.5197	1.5134	McCaulay	[d]
	Corrected m.p. in °C. Detd.	Corrected m.p. in °C. Lit.				
Pentamethylbenzene	51.6–51.9	53.0			McCaulay	[f]
Durene	79.1–79.3	79.7			McCaulay	[g]
Hexamethylbenzene	165.1–166.0	165.3			McCaulay	[e]

[a] The reported values of boiling and melting points and the indices of refraction were all taken from Egloff's "Physical Constants of Hydrocarbons." His weighted mean values were used whenever available. [b] Values of 1.4912, 1.4953, 1.4967 and 1.4996, have been reported at 20.0°. [c] The original sample obtained from McCaulay had been prepared by distilling a mixture of Eastman Kodak Co. trimethylbenzenes and selecting a 167–171° cut. Infrared analysis showed this cut to contain about 95% pseudocumene (169°), 3% mesitylene (165°), 0.5% hemimellitene (176°) and 1.5% of mixed ethyltoluenes (*o*-, 165°, *m*-, 159°, *p*-, 163°). [d] The original sample was 99% pure as checked by infrared analysis by McCaulay. It had been prepared by extracting a tetramethylbenzene mixture with HF–BF_3. [e] Prepared by McCaulay from pentamethylbenzene by the Jacobsen reaction. [f] The original sample had been obtained by McCaulay from Eastman Kodak Co. and was estimated by him to be 99% pure. [g] Obtained from the Edcan Laboratories by McCaulay and estimated by him to be 99% pure.

with a measured quantity of the pure acid. The solution withdrawn was then discarded and the cell contents remixed.

To each of the solutions in the cell, or to the final dilution made up by means of the mixing buret, increments of boron trifluoride were added through V_8 up to a total pressure of about 100 lb. per sq. in., or until there was no further change in the conductance. From the known volume of the cell, together with the total pressure and total amount of gas admitted, the concentration of the boron trifluoride in the liquid phase was calculated. It is estimated that the concentrations of the boron trifluoride were known to at least 1%.

Purification of the Other Reagents Used.—The boron trifluoride was purified from the commercial product obtained from the Harshaw Chemical Company according to the method of Brown and Johannesen.[10] It was analyzed chemically using the procedure of Swinehart, Bumbles and Flisik.[11] The components found before and after purification, respectively, were: SO_2, 0.10%, 0.00%; SiF_4, 0.74%, 0.17%; BF_3, 97.6%, 99.1%. Its vapor pressure at −111.8° was 300 mm. which is the same as reported by Brown and Johannesen.[10] The determination of the compressibility of boron trifluoride up to a 1000 lb. per sq. in. will be discussed in a later paper.

The liquid hydrocarbons used in this study were all fractionated through a Podbielniak column. The Podbielniak was an 8-mm. by 12-in. Heligrid packed column operated at an efficiency of about 50 plates. In the case of benzene and toluene, the samples were first shaken with concentrated sulfuric acid, then washed and dried before distilling. The mid-fractions of each of the liquids were collected over a range of ±0.1° or less. The refractive index for each liquid was measured on an Abbe refractometer at 25.0 ± 0.1°. The solid hydrocarbons were recrystallized from purified benzene and dried overnight under vacuum. The products were crystalline white solids. The melting points were determined in capillary tubes in a carefully heated oil-bath. Both the liquids and the solids were stored in tightly closed bottles in desiccators over drierite. The physical constants[12] for these compounds are given in Table II.

The potassium fluoride was prepared by drying Mallinckrodt Analyzed $KF \cdot 2H_2O$ in a waxed bottle in a desiccator under high vacuum overnight. The salt was then ground rapidly to a fine powder in an agate mortar and dried again for several days before use.

Experimental Results and Discussion

Conductances in Hydrofluoric Acid.—The equivalent conductances of the entire series of methyl substituted benzenes and of potassium fluoride as a function of concentration in anhydrous hydrofluoric acid, are given in Table III. The estimated overall accuracy of these measurements was 3%. The equivalent conductances were calculated using the relationship

$$\Lambda = 1000L/c \qquad (2)$$

where L was the specific conductance of the compound at an equivalent concentration c. Since the densities of the solutions involved were unknown, the concentrations used were all molal concentrations m, that is, moles of solute per 1000 g. of solvent. There was probably no appreciable error involved, since the density of the pure solvent is 0.98. The specific conductance used was the difference between the measured specific conductance L_m, and the specific conductance of the pure solvent L_s, that is

$$L = L_m - L_s \qquad (3)$$

This relationship would be true only if there was no measurable interaction between the solvent and the

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(10) H. C. Brown and R. B. Johannesen, THIS JOURNAL, **72**, 2935 (1950).

(11) C. F. Swinehart, H. R. Bumbles and H. Flisik, *Anal. Chem.*, **19**, 28 (1947).

(12) G. Egloff, "Physical Constants of Hydrocarbons," Reinhold Publ. Corp., New York, N. Y., 1939.

solute. However, as will be shown later, this is not the case here. The treatment of systems of this type has been described by Davies[13] and by Wynne-Jones.[14] Actually, a large part of the solvent conductance was due to the presence of traces of water and of salts. This solvent conductance varied for each measurement, so to obtain consistent conductance values in the absence of quantitative knowledge of the solvent equilibrium, relationship 3 was used. The specific conductances, L_m and L_s, were calculated from the corresponding measured resistance in ohms, and the cell constant, 4.90 cm.$^{-1}$.

TABLE III

EQUIVALENT CONDUCTANCE AND DISSOCIATION CONSTANT OF COMPOUNDS IN HYDROFLUORIC ACID AT 20°

Compound	Molality	Equivalent conductance	Dissociation[h] constant	Equiv. cond. in excess BF_3
Benzene	0.0868	2.3	4.2×10^{-8}	...[a]
	.216	0.65	0.82×10^{-8}	...
	.442	0.32	0.41×10^{-8}	...
Toluene	0.0702	6.3	2.6×10^{-7}	245[b]
	.181	2.8	1.97×10^{-7}	182
	.3035	0.50	0.069×10^{-7}	166
p-Xylene	0.0585	9.1	4.5×10^{-7}	266
	.0833	6.7	3.55×10^{-7}	209
	.134	5.2	3.4×10^{-7}	205
	.167	4.55	3.3×10^{-7}	225
o-Xylene	0.0595	7.9	3.5×10^{-7}	267
	.148	5.4	4.1×10^{-7}	219.5
	.292	3.7	3.85×10^{-7}	185.5
m-Xylene	0.0524	40.9	9.5×10^{-6}	294.5
	.172	18.3	6.2×10^{-6}	235.5
	.364	7.0	1.8×10^{-6}	205
Pseudocumene	0.0532	54.5	1.85×10^{-5}	271
	.1105	41.4	2.2×10^{-5}	234
	.207	27.8	1.9×10^{-5}	197
Hemimellitene	0.0541	65.3	2.8×10^{-5}	278
	.117	38.3	2.0×10^{-5}	221
	.238	23.2	1.5×10^{-5}	208.5
Mesitylene	0.0545	299	2.9×10^{-3}	272
	.0857	279	4.4×10^{-3}	254
	.156	218	3.8×10^{-3}	204.5
	.204	223	8.4×10^{-3}	218
	.275	194	8.6×10^{-3}	202
Durene	0.0147	245[c]	2.1×10^{-4}	...
	.0147	398[d]	...	...
	.0209	194[c]	1.5×10^{-4}	...
	.0324	61.7[e]	0.14×10^{-4}	273
Prehnitene[c]	0.0595	129	1.7×10^{-4}	272
	.0640	117	1.4×10^{-4}	...
	.0920	102	1.5×10^{-4}	250
	.132	78.0	1.2×10^{-4}	238.5
	.1995	55.5	0.88×10^{-4}	197
Isodurene	0.0491	322	4.1×10^{-3}	280
	.0568	314	4.4×10^{-3}	275
	.0580	290	2.7×10^{-3}	243
	.0880	259	3.0×10^{-3}	...
	.1113	252	4.1×10^{-3}	...
	.162	264	16×10^{-3}	224
	.1905	250	17×10^{-3}	212.5
	.206	221	8.2×10^{-3}	...
Pentamethylbenzene	0.0141	362	1.3×10^{-3}	...
	.0169	...	...	314
	.0413	340	4.8×10^{-3}	280
	.0789	312	9.4×10^{-3}	...
	.148	284	28×10^{-3}	...
Hexamethylbenzene	0.00609	...	...	345[f]
	.0181	412	2.7×10^{-2}	...
	.0304	397	8.6×10^{-2}	...
	.0380	...	...	335
	.0725	349.5	6.3×10^{-2}	...
	.1374	297	4.3×10^{-2}	...
Potassium fluoride	0.1035	346	...	263
	.201	291	...	...
	.371	263	...	...
	.0512[g]	393	...	313
	.106	338	...	...
	.212	292	...	...

[a] Even at the highest pressures used the complex was nowhere near being completely dissociated. [b] The conductances did not quite correspond to complete dissociation even at the highest pressures. [c] All measurements taken with prehnitene and durene drifted with time. In the case of prehnitene the readings recorded were extrapolated back to zero time, but in the case of durene, this was not possible, since it required about an hour to dissolve the solid even with vigorous stirring in the small buret. The two durene values of conductance reported were values after isomerization had proceeded for about an hour. [d] This conductance was measured after the solution had remained in the cell overnight, at which time the resistance was constant. [e] This solution was made up by dissolving the solid in cyclohexane and introducing the solution directly into the cell. The initial reading is given. [f] This was measured in the presence of cyclohexane which also contributed to the conductance. [g] An independent set of dilutions were made on a new sample of potassium fluoride alone in hydrofluoric acid. [h] Calculated by equations 8 and 9.

Conductances and Vapor Pressures in HF–BF_3 Mixtures.—The specific conductances of all of the compounds were measured as a function of boron trifluoride concentration. Examples of the two general types of curves obtained are given in Figs. 4 and 5. For each increment of BF_3 the total pressure of the system was also recorded so that the concentration of BF_3 in the liquid phase could be calculated. These vapor pressure results were essentially the same as reported by McCaulay and Lien.[4]

The shape of all of these curves can be correlated directly with the basic character of the aromatic hydrocarbon. In Table III we observe that the equivalent conductance at any one concentration increases in going from benzene to hexamethylbenzene, that is, the ionic concentration must be increasing. Since increasing methyl substitution increases the electron donating ability of the aromatic ring, and hence its basic character, the increase in the number of ions is reasonable. The conductance curves rise steeply with decreasing concentration which is usually characteristic of a weak electrolyte in a medium of high dielectric constant, while the conductance curves in Fig. 3 approach the Onsager slope as will be shown later.

The specific conductance curve in Fig. 4 is typical of many of the compounds studied. In general, as boron trifluoride was added, the conductance

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(13) C. W. Davies, "The Conductivity of Solutions," John Wiley and Sons, Inc., New York, N. Y., 1930.

(14) W. F. K. Wynne-Jones, *J. Phys. Chem.*, **31**, 1647 (1927).

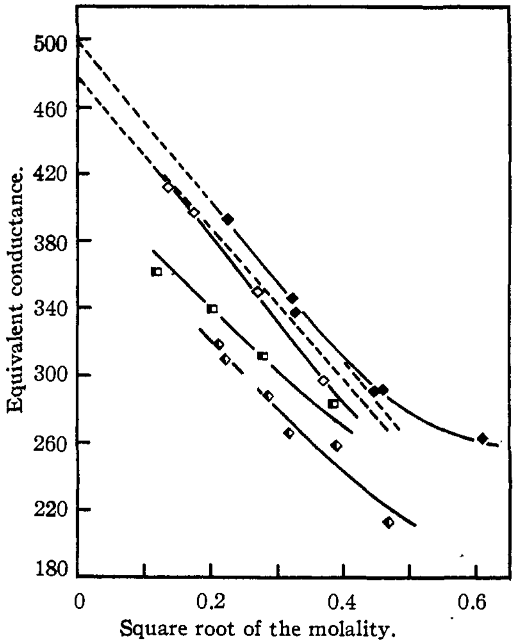

Fig. 3.—Equivalent conductance of $ArH^+ \cdot F^-$ in hydrofluoric acid: ■□, pentamethylbenzene; ◇, hexamethylbenzene; ◆, potassium fluoride; ◆▷, potassium fluoborate. -----, Onsager limiting slopes.

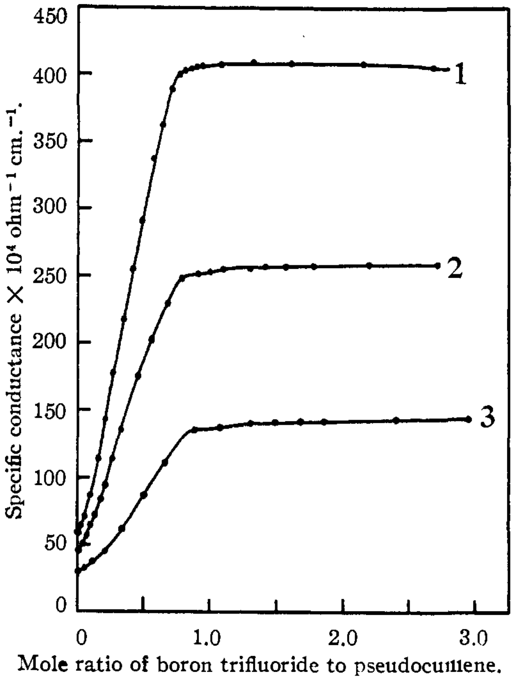

Fig. 4.—Specific conductance of pseudocumene in hydrofluoric acid in the presence of boron trifluoride: curve 1, 0.207 molal; curve 2, 0.111 molal; curve 3, 0.0532 molal.

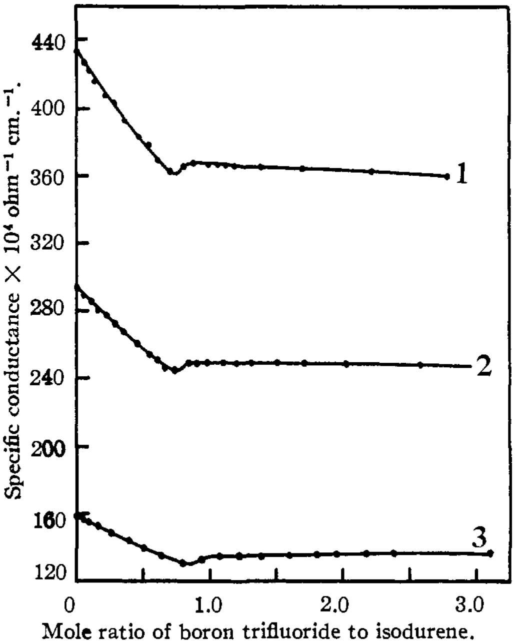

Fig. 5.—Specific conductance of isodurene in hydrofluoric acid in the presence of boron trifluoride: curve 1, 0.162 molal; curve 2, 0.117 molal; curve 3, 0.0491 molal.

increased gradually until one mole of boron trifluoride per mole of hydrocarbon had been added, and then leveled off. As more boron trifluoride was added, the conductance slowly started to fall. This is not shown because it usually did not occur until a mole ratio of about three was reached. The sharpness of the change in slope of the curve near the 1:1 mole ratio of boron trifluoride to aromatic depended on the degree of methyl substitution and on the meta orientation of the methyl groups in the same way as before. However, for mesitylene, isodurene, pentamethylbenzene and hexamethylbenzene, as well as for potassium fluoride, the conductance initially decreased to a minimum, and then rose slightly before leveling off. The minimum occurred before, or at, a 1:1 mole ratio of boron trifluoride to aromatic or to potassium fluoride. In many of these curves there was a small but sharp rise in the conductance before a mole ratio of 2:1 was reached. It amounted to only a few per cent. Its possible significance will be discussed at a later date. The effect of traces of water in the solvent on these conductance curves was not noticeable. It was presumed that the first portion of boron trifluoride added removed any water present by the reaction

$$BF_3 + H_2O \rightleftarrows BF_3 \cdot H_2O \qquad (4)$$

Discussion of the Equilibria Involved.—We have just seen that all of the data were consistent with the view that the methylbenzenes were acting as weak bases in reference to HF as the acid. The logical acid–base equilibrium to be assumed would be

$$Ar + HF \rightleftarrows ArH^+ + F^- \qquad (5)$$

This same equilibrium was suggested by Hammett[15] to account for the solubility of aromatic hydrocarbons in HF, and by McCaulay and Lien.[4] We can therefore say that equilibrium 5 is the principal equilibrium involved in these systems.

The position of equilibrium 5 has been shown to depend on the degree of methyl substitution and on the orientation of the substituents, both of which determine the basic character of the aromatic nucleus by changing the electron donating ability of the molecule. The results just presented on the

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(15) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 294.

addition of boron trifluoride to the solutions of aromatics substantiate the existence of an equilibrium depending on the basicity of the aromatic but in addition show that one mole of aromatic interacts per mole of boron trifluoride and of hydrofluoric acid. It was assumed that the addition of BF_3 established a second equilibrium in addition to 5, namely

$$F^- + BF_3 \rightleftarrows BF_4^- \qquad (6)$$

Further proof of the existence of this equilibrium and the calculation of its equilibrium constant will be discussed in a later paper. The addition of BF_3 to solutions of aromatics in hydrofluoric acid therefore shifts equilibrium 5 to the right by the replacement of F^- ions by BF_4^- ions which increases the total ion concentration and therefore increases the conductance. This accounts for the rise in conductance on the addition of boron trifluoride as illustrated in Fig. 4. If equilibrium 5 already lies far to the right, the addition of boron trifluoride will cause very little increase in the total number of ions in solution since equilibrium 6 merely changes the ionic species from F^- to BF_4^-. We might expect the mobility of this fluoborate ion to be much less than that of the fluoride ion and therefore a decrease in conductance will occur on the addition of boron trifluoride to such solutions. This actually happened in the case of mesitylene, isodurene, pentamethylbenzene and hexamethylbenzene, to give results as illustrated in Fig. 5. This same type of conductance curve was also observed for potassium fluoride. Further work is planned to explain the minimum which occurs in these curves.

It is apparent from Figs. 4 and 5 that sufficient BF_3 could be added in most cases to completely shift equilibrium 5 to the right, that is, boron trifluoride could be added until the conductance was constant. Under these conditions, the ArH^+ and BF_4^- ions would be the only ones present in appreciable concentration and the conductance would correspond to the completely dissociated species ArH^+ and BF_4^-. These conductances are listed in Table III. We would expect then that a plot of these equivalent conductances of the aromatics in hydrofluoric acid with sufficient excess of boron trifluoride to shift equilibrium 5 completely to the right would give identical curves for all of the aromatics, except for differences due to the different mobilities of the aromatic cations. Such a plot is shown in Fig. 6. This indicates that the mobility of the toluene cation cannot be greatly different than the mobility of the hexamethylbenzene cation $HexH^+$. The values for benzene were not obtainable within the limits of pressure of boron trifluoride used, and the values for toluene, although plotted in Fig. 6 are low for the same reason. That is, equilibrium 5 was not shifted completely to the right as evidenced by the fact that the specific conductance curves did not become horizontal up to the highest pressure used. No explanation is offered for the high values for *m*-xylene in Fig. 6.

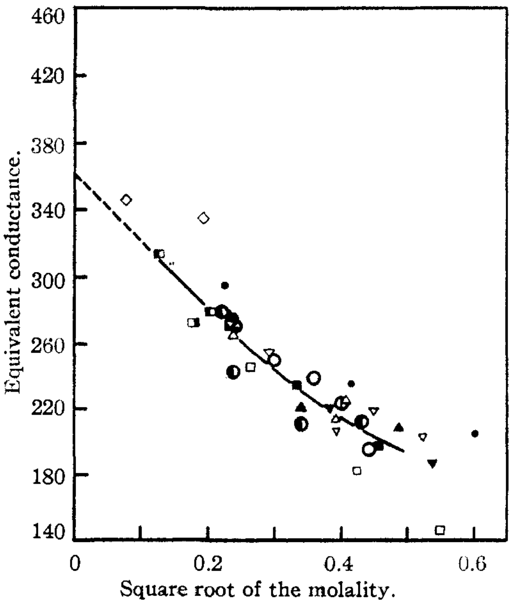

Fig. 6.—Equivalent conductance of $ArH^+ \cdot BF_4^-$ in hydrofluoric acid: □, toluene; △, *p*-xylene; ▼, *o*-xylene; ●, *m*-xylene; ■, pseudocumene; ▲, hemimellitene; ▽, mesitylene; ○, prehnitene; ◐, isodurene; ◨, durene; ◧, pentamethylbenzene; ◇, hexamethylbenzene.

It was interesting to compare the slope of these experimental conductance curves for the completely dissociated species ArH^+ and BF_4^- with the theoretical limiting Onsager slopes, even though the concentrations involved were well outside of the range of validity of the simple Onsager equation. The constants were evaluated from the viscosity data of Simons and Dresdner[16] and from the dielectric constant data of Fredenhagen and Dahmlos.[17] At 20.0° the limiting Onsager equation for a 1 : 1 electrolyte becomes

$$\Lambda = \Lambda_0 - (0.348\Lambda_0 - 285)\sqrt{c} \qquad (7)$$

There are no data available on limiting ionic conductances in hydrofluoric acid from which we could independently evaluate Λ_0 so that the theoretical slope could be evaluated. Instead the curves in Figs. 3 and 6 were extrapolated to zero concentration as indicated by the dotted lines. An extrapolation from these concentrations was open to considerable question, but from these limiting conductances, the theoretical slopes were calculated. They agreed to within 5% with the experimental slopes. This lends some justification to the procedure used in these calculations.

Calculation of the Equilibrium Constants.—The stoichiometric equilibrium constant expression for equilibrium 5 is

$$K = (F^-)(ArH^+)/(Ar)(HF) \qquad (8)$$

or in terms of the degree of association

$$K = c\alpha^2/(1 - \alpha)(50.0) \qquad (9)$$

where

$$\alpha = \Lambda/\Lambda' \qquad (10)$$

and 50.0 is the molal concentration of the solvent, hydrofluoric acid. This was constant within experimental error throughout all of the experiments. Λ' would be the equivalent conductance at the existing ion concentration if complete dissociation had

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[16] J. H. Simons and R. D. Dresdner, THIS JOURNAL, **66**, 1070 (1944).

[17] K. Fredenhagen and J. Dahmlos, *Z. anorg. allgem. Chem.*, **178**, 272 (1928).

existed. The curve for the complete dissociation of all the species, $ArH^+ \cdot F^-$, was given by the Onsager curve for hexamethylbenzene of Fig. 3. By choosing this curve, it was assumed that hexamethylbenzene was completely dissociated in the more dilute solutions studied. In the previous discussion it was shown that the simple Onsager equation was obeyed in this system up to about 0.15 molal, and also that the mobilities of all of the cations ArH^+ were the same within experimental error. Therefore it was reasonable to use this theoretical curve of hexamethylbenzene in Fig. 3 to evaluate Λ' and therefore α. The value of α was actually calculated by successive approximations using $\Lambda' = \Lambda_0$ to calculate the first approximation to the ion concentration. The second approximation to Λ' was found from the dotted curve of Fig. 3 for hexamethylbenzene at the first approximation to the ion concentration. This process was continued until α was constant. These constants for each of the solutions are given in Table III, and plotted in Figs. 7 and 8. In Table I are listed the values of the relative basicities at 0.1 molal concentration of the methylbenzene. These were calculated from the equivalent conductance values from the smooth curves of the data. These relative basicities, when compared with the values of McCaulay and Lien, gave the same order of basic strength but the actual values are quite different as might be expected from the differences in our experimental conditions. McCaulay and Lien made their measurements on solutions having a higher concentration of aromatic, in the presence of boron trifluoride, and at lower temperatures than our measurements.

Of all of the methylbenzenes measured in anhydrous hydrofluoric acid only the conductances of prehnitene and of durene changed with time. There was no change with time in the conductances of the xylenes or the trimethylbenzenes. The conductances of prehnitene and durene approached that of isodurene and if allowed to stand overnight actually attained that of isodurene. This would tend to indicate that prehnitene and durene isomerize almost entirely to isodurene. The addition of boron trifluoride increased the rate of change of conductance markedly. From preliminary measurements it appears that the rate of isomerization of prehnitene does not follow a first-order rate law.

The question arose as to why there was no noticeable change with time in the conductances of the xylenes, the trimethylbenzenes and of pentamethylbenzene in hydrofluoric acid. There are two ways of answering this question. If the driving force is the basicity of the aromatic then it would be expected that the dimethyl- and trimethylbenzenes, which are less basic than the tetramethylbenzenes, would isomerize much more slowly or not at all. However, the addition of a reagent such as boron trifluoride, which shifts equilibrium 5 toward the ionic species, should speed up or initiate these isomerizations. There was no method of detecting these isomerizations conductimetrically and no analyses were made on the solutions removed from the conductance cell so that no test was made of this last postulate. McCaulay[18] reported that the xylenes do not isomerize at a noticeable rate until one mole of boron trifluoride has been added per mole of aromatic. The isomerization of the methylbenzenes in anhydrous hydrofluoric acid will be the subject of a later paper. It is of interest to note here that in the Jacobsen rearrangement the end-product is always the vicinal configuration in contrast to the symmetric configuration for isomerizations in hydrofluoric acid.

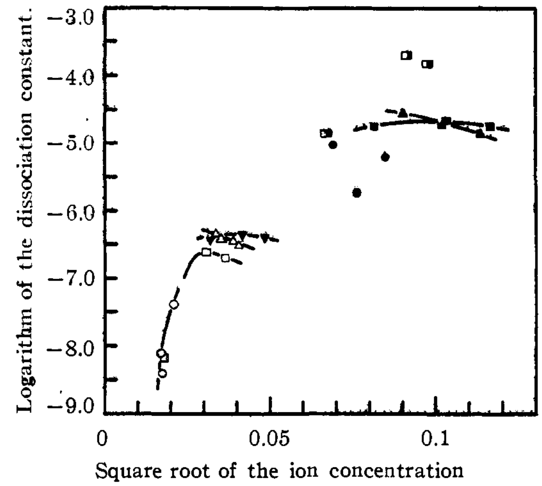

Fig. 7.—The dissociation constants of the methylbenzenes in hydrofluoric acid: O, benzene; □, toluene; Δ, *p*-xylene; ▼, *o*-xylene; ●, *m*-xylene; ■, pseudocumene ▲, hemimellitene; ◘■, durene (during isomerization).

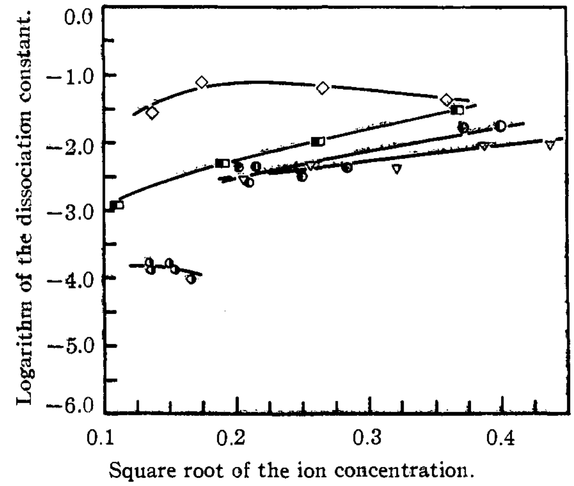

Fig. 8.—The dissociation constants of the methylbenzenes in hydrofluoric acid: ∇, mesitylene; ◐, isodurene; ◑, prehnitene; ■□, pentamethylbenzene; ◇, hexamethylbenzene.

We have shown that the cation ArH^+ often exists in hydrofluoric acid solutions in high concentrations. This species was postulated to be the intermediate in isomerizations of aromatics occurring in this medium. That is, a high concentration of ArH^+ ion favors the formation of the corresponding carbonium ions which then isomerize to the configuration of the product. On the basis of the similarity between the aluminum halide–halogen acid system and the boron trifluoride–hydrofluoric acid system, we may assume that this species is also the intermediate in similar isomerization reactions cat-

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[18] D. A. McCaulay, private communication, 1951.

alyzed by an aluminum halide and a halogen acid. This is substantiated by more recent work, which showed that the halide acid was essential to these isomerizations, and also by the fact that the aromatic products which are the strongest bases are favored. This cation, ArH$^+$, has not been identified in the aluminum halide–halogen acid catalyst systems since the reactions are usually carried out in a neutral or aromatic medium where the equilibrium

$$\text{Ar} + \text{HX} \rightleftarrows \text{ArH}^+ + \text{X}^- \qquad (11)$$

would be almost entirely to the left, and where the low dielectric constant of the solvent would not favor the formation of ionic intermediates in appreciable concentration.

The recent work of Brown and Pearsall[3] tends to substantiate this viewpoint. They postulate that when the complex phase appears in a Friedel–Crafts type reaction, the formation of ionic intermediates is facilitated. This accounts for the greatly increased rate of reaction as soon as this second phase appears. Since this paper was submitted, Brown and Brady have given a more detailed presentation of their viewpoint.[19]

Acknowledgment.—The authors are indebted to D. A. McCaulay of Standard Oil Company of Indiana for supplying us with many of the methylbenzenes used.

[19] H. C. Brown and J. D. Brady, THIS JOURNAL, **74**, 3570 (1952).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF PENNSYLVANIA AND THE DEPARTMENT OF CHEMISTRY OF ILLINOIS INSTITUTE OF TECHNOLOGY]

The Dissociation Constants of Acids in Salt Solutions. I. Benzoic Acid

BY MARTIN KILPATRICK[1]

RECEIVED AUGUST 4, 1952

With the increased use of the "swamping-salt" principle for kinetic and equilibrium studies, experimental determinations of the dissociation constants of acids in various solvent salts are needed. The present paper reports the dissociation constant of benzoic acid in water for three solvent salts and the dissociation constant in methyl and ethyl alcohol and ethylene glycol for the solvent salt lithum chloride.

In connection with kinetic and acid strength studies in the author's laboratory, many determinations of the dissociation constant of benzoic acid in aqueous and non-aqueous salt solutions have been accumulated. This paper presents a summary of these results together with a calculation of the activity coefficients.

Most of the measurements were made with the cell

$$\begin{array}{c|ll||l||ll|c} & \text{HB} & 0.005\,M & & & & \\ \text{Au} & \text{MB} & 0.005\,M & \text{MCl} & \text{HCl} & 0.005\,M & \\ & & & 1.00\,M & \text{MCl} & X\,M & \text{Au} \\ & \text{MCl} & X\,M & & & & \end{array}$$

Quinhydrone Quinhydrone

where $X \geqq 0.045M$

as reported by Elliott and Kilpatrick,[2] while the others were made with a similar cell described by Kilpatrick and Chase.[3] Within the assumptions involved, the electromotive force method gives the ratio of the hydrogen ion concentrations in the two halves of the cell, and if we assume that the hydrogen ion concentration is equal to the stoichiometric concentration of the strong acid, the usual concentration dissociation constant can be calculated from the known stoichiometry of the buffer solution

$$K_c = C_{H_3O^+}\frac{C_{B^-}}{C_{HB}} \qquad (1)$$

where the concentration of water is included in the constant. Table I summarizes the results for the aqueous salt solutions of alkali chlorides. Since

$$K_a = K_c\frac{f_{H^+}f_{B^-}}{f_{HB}} \qquad (2)$$

and $K_a = 6.32 \times 10^{-5}$,[4] and the salting-out constants for benzoic acid are known,[5] the mean activity coefficient of the ions of benzoic acid can be calculated. The ratio K_c/K_a, the activity coefficient of molecular benzoic acid f_{HB}, and the mean activity coefficient of the ions of benzoic acid $\sqrt{f_{H^+}f_{B^-}}$ are given in Table II.

TABLE I

THE DISSOCIATION CONSTANT OF BENZOIC ACID IN AQUEOUS SALT SOLUTIONS AT 25°, $K_c \times 10^5$

Moles/ liter	Electrolyte KCl	NaCl	LiCl
0.05	9.10	9.12	9.16
.10	10.08	10.05	11.08
.20	10.43	10.81	11.47
.30	10.83	11.38	11.86
.40	11.18	11.79	12.93
.50	11.32	11.90	12.95
.60	11.38	11.85	13.00
.70	11.12	11.80	12.95
.80	11.06	11.72	12.94
.90	11.10	11.55	12.90
1.00	10.79	11.36	12.88
1.50	9.94	10.48	12.60
2.00	8.84	9.20	11.25
2.50	7.58	7.58	9.46
3.00	6.52	6.49	8.99

Table III presents the dissociation constant of benzoic acid in the solvents methyl and ethyl alcohol and ethylene glycol, at total ion concentrations of 0.05 and 0.10 molar for LiCl from e.m.f. measurements against HCl in the same solvent salt. The values for the dissociation constant at zero electro-

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[1] Illinois Institute of Technology.

[2] J. H. Elliott and M. Kilpatrick, *J. Phys. Chem.*, **45**, 454 (1941).

[3] M. Kilpatrick and E. F. Chase, THIS JOURNAL, **53**, 1732 (1931).

[4] F. G. Brockman and M. Kilpatrick, *ibid.*, **56**, 1483 (1934).

[5] A. Osol and M. Kilpatrick, *ibid.*, **55**, 4430 (1933).