0.1 M electrolyte solutions and not in distilled water.

Acknowledgment is made to the Graduate School of the University of Minnesota for a grant which enabled us to carry out this investigation.

Summary

1. When electrically disconnected mercury drops into air-saturated water or when mercury connected with a pool of mercury drops into air-free water an abnormally large drop time is found.

The drop of mercury remains attached to the glass. The abnormal behavior becomes more pronounced the smaller is the bore of the capillary. The results obtained with an abnormally dropping capillary are badly reproducible and depend greatly on the degree of inclination of the capillary.

2. The abnormal behavior has been interpreted on the basis of interaction between the electric double layers at the glass and at the mercury–aqueous phase interfaces.

Studies in Stereochemistry. II. Steric Strains as a Factor in the Relative Stability of Some Etherates of Boron Fluoride

BY HERBERT C. BROWN AND RICHARD M. ADAMS[1]

Modern physical techniques for studying gaseous molecules have contributed much information regarding molecular configurations.[2,3] In the main, these later results have confirmed those of the early workers in stereochemistry who drew their conclusions from isomer number and chemical reactions. In many instances, however, detailed data on atomic dimensions and valence angles and the careful study of small irregularities in the physical and chemical properties of substances has made possible some interesting extensions of the classical principles of stereochemistry.

One recent extension of this kind is based on evidence that steric interference between two groups may weaken considerably the bond joining the groups. To illustrate, the per cent. dissociation of the tetraaryldialkylethanes and the dixanthyldialkylethanes increases with increasing size of the alkyl group[4]; and the ortho methyl groups of sym-tetraphenyldi-o-tolylethane increase the dissociation into free radicals more than do the methyl groups of the corresponding meta or para derivatives (25% vs. 5%).[5]

Unfortunately, these examples are not entirely satisfactory. The molecules are large and complicated; moreover, interpretation of the results is made particularly hazardous by the fact that resonance plays an important part in the dissociation of such ethane derivatives. It would be highly desirable to have more substantial evidence of this same effect in simpler molecules in which resonance is not important. Recently, such examples of unmistakable weakening of bonds by steric strains have been found.[6] A study of the relative stability of some coördination compounds of borine, boron fluoride and trimethylboron with amines revealed that trimethylamine is a stronger base (in the generalized Lewis sense[7]) than pyridine toward the acids hydrogen chloride, borine and boron fluoride, but that the reverse is true when trimethylboron is used as the reference acid.

This "anomalous" result is apparently due to steric strains, for molecular models reveal that in the compounds studied considerable steric interference is to be expected only in trimethylamine-trimethylboron.[8,9]

There are reasons to believe that such steric strains are more common than has been supposed

(1) This paper is taken from a dissertation submitted by Richard M. Adams to the Faculty of the Division of the Physical Sciences of the University of Chicago, in partial fulfillment of the requirements for the degree of Master of Science.

(2) Stuart, "Molekülstruktur," Julius Springer, Berlin, 1934.

(3) Pauling, "The Nature of the Chemical Bond," 2nd ed., Cornell University Press, Ithaca, N. Y., 1940.

(4) Conant and Bigelow, THIS JOURNAL, **50**, 2041 (1928); Conant, Small and Sloan, ibid., **48**, 1743 (1926).

(5) Marvel, Mueller, Himel and Kaplan, ibid., **61**, 2777 (1939).

(6) Brown, Schlesinger and Cardon, ibid., **64**, 325 (1942).

(7) Lewis, J. Franklin Inst., **226**, 293 (1938).

(8) For a discussion of the nomenclature used for these coördination compounds, see Davidson and Brown, THIS JOURNAL, **64**, 316 (1942), footnote 11.

(9) It was pointed out that steric strains present in trimethylamine-trimethylboron must be duplicated in its isostere, hexamethylethane, since the dimensions and configurations of the two molecules are almost identical.[4] It is of considerable interest that in a recent electron-diffraction study of this hydrocarbon, Bauer and Beach [ibid., **64**, 1142 (1942)] find evidence that the central C–C bond is stretched (1.58 vs. 1.54 Å.).

and that they play a far more important role in determining the physical and chemical properties of substances than has hitherto been realized. It appears highly desirable to obtain more information concerning the existence and magnitude of these effects. Accordingly, a study was made of the addition compounds between boron fluoride and some representative aliphatic ethers (methyl ether, ethyl ether, isopropyl ether and tetrahydrofuran). Particular attention was given to the effect of steric strains on the relative ease with which the addition compounds dissociate.

Experimental Part

Apparatus and Methods.—The high vacuum apparatus shown in Fig. 1 was constructed and used in the preparation and study of the etherates of boron fluoride. The materials were introduced into the apparatus through the tube opener, TO, and condensed in the desired section of the apparatus (e. g., in the storage bulbs, SB) with aid of liquid nitrogen. The starting materials were purified by fractional distillation and fractional condensation in the fractionation system, FS. The homogeneity of the substances used in this investigation was usually established by vapor pressure measurements. (In some cases purification by distillation outside the vacuum system was relied upon.) The vapor pressure of the more volatile substances could be measured satisfactorily on the manometers, M_1 and M_2, in the fractionation system, FS. The vapor pressures of the less volatile substances were studied in the apparatus HTB (high temperature bulb).[10]
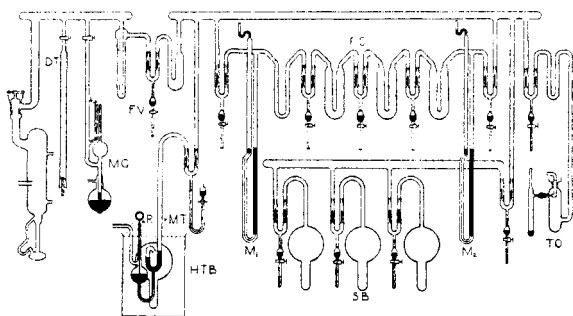

Fig. 1.—Diagram of apparatus.

This apparatus (HTB) was used as follows. The material was condensed in the apparatus with liquid nitrogen, the mercury was allowed to rise in the tube, MT, by raising the rod, R, thus shutting the flask off from the rest of the vacuum line. The entire apparatus was immersed in a heated bath and the pressures read with a cathetometer. The bath was constructed from a 3-liter beaker carefully selected for freedom from striations. The sides of this beaker were insulated with several layers of asbestos paper, but a narrow section opposite the manometer was left uncovered to serve as a window for observing the pressure. A close-fitting asbestos lid covered the beaker, which rested on a heavy copper plate heated with a gas

(10) Burg and Schlesinger, THIS JOURNAL, **59**, 785 (1937).

flame. An air-driven stirrer kept the bath liquid (either water or paraffin oil) well stirred. With this bath the temperature could be maintained constant for periods of time more than sufficient for the purposes of the investigation.

Preparation and Study of the Etherates of Boron Fluoride.—The usual procedure for the preparation of the etherates of boron fluoride was to condense equal volumes (measured as gases under standard conditions)[11] of the ether and boron fluoride in the high temperature bulb, HTB. Very shortly after the liquid nitrogen was removed, the components reacted to form the addition compound.

The flask was heated by means of the bath previously described and the saturation pressures of the complex noted. After a series of measurements had been completed, a portion of the compound was removed to another part of the apparatus, and the observations were repeated on the portion remaining. The reproducibility of the values observed was taken as satisfactory evidence of the homogeneity of the products.

The degree of dissociation of the addition compounds $(R_2O:BF_3 \rightleftarrows R_2O + BF_3)$ over a range of temperatures was studied in the same apparatus, HTB. Equal volumes of ether and boron fluoride were introduced into the flask and the pressures observed over a range of temperatures. Since the size of the samples introduced was selected so that the total pressure would be considerably below the saturation pressure of the complex, the degree of dissociation, α, could be calculated from the ratio of the observed pressure to the pressure calculated assuming no dissociation. The equilibrium constant at each temperature was then calculated from the value of α by the use of the equation

$$K_p = \alpha^2 P/(1 - \alpha^2)$$

The free energy change, ΔF, was calculated from the equilibrium constant

$$\Delta F = -RT \ln K$$

Finally, from the variation in K with temperature, ΔH could be calculated by the well-known thermodynamic equation

$$\Delta H = RT^2 \frac{d \ln K}{dT}$$

Since the etherates of boron fluoride dissociate almost completely at temperatures where the saturation pressures of the complexes are high, it was necessary to work at comparatively low pressures (10–30 mm.). Preliminary experiments indicated that it was possible to measure pressures over a considerable range of temperature to better than 0.1 mm. This accuracy was considered satisfactory. The observed readings were, of course, corrected for the density of mercury and its vapor pressure (the latter correction was necessary because one limb of the manometer was open to a high vacuum).

Results

Methyl Ether–Boron Fluoride, $(CH_3)_2O:BF_3$. —The addition compound, methyl ether–boron fluoride, was prepared by the reaction of 12.5 cc. of

(11) All volumes given in this paper refer to gases at standard conditions.

boron fluoride (p = 309 mm. at $-111.6°$)[12] and 12.4 cc. of methyl ether (p = 119.6 mm. at $-60°$)[13] at a low temperature. The product was a white solid which melted to a colorless liquid at -14 to $-12°$. The saturation pressure data of the complex are given in Table I and represented graphically in Fig. 2-A. It has been previously reported

TABLE I

SATURATION PRESSURES OF METHYL ETHER–BORON FLUORIDE

Temp., °C.	0	10	15	20	30	40
Press., mm.	0.9	1.6	2.3	3.0	6.1	9.5
Temp., °C.	50	60	70	80[a]	90[a]	98.5[a]
Press., mm.	17.2	31.2	52.7	90.3	144.3	179.0

[a] The measurements from 80° on were made on a larger sample, prepared from 38.0 cc. each of methyl ether and boron fluoride.

that the "boiling point" of the complex is 126–8°.[14] Extrapolation of the saturation pressure curve to 760 mm. yields a value of 127° for the "boiling point." This is not a true "boiling point," since at this temperature the complex is practically completely dissociated into its components, methyl ether and boron fluoride.

The dissociation of the complex was studied over a range of temperatures in the manner previously described. Methyl ether, 5.83 cc., and 5.83 cc. of boron fluoride were condensed in the high temperature bulb (volume, 247.6 cc.) and permitted to react. The apparatus was then heated to a temperature at which the total pressure was below the saturation pressure of the complex and observations made over a range of temperatures. The results are summarized in

TABLE II

DISSOCIATION PRESSURES OF METHYL ETHER–BORON FLUORIDE

Temp., °C.	Pressure observed, mm.	Pressure calculated, mm.	Degree of dissociation, α	Dissociation constant, K (atm.)
66	36.2	22.4	0.631	0.032
70	37.4	22.5	.662	.038
73	38.2	22.7	.682	.044
75.5	39.1	22.9	.707	.051
78.5	40.2	23.0	.748	.067
81	40.7	23.2	.754	.071
83.5	41.4	23.4	.769	.079
86	42.1	23.5	.791	.091
89	43.0	23.7	.814	.111
93	44.0	24.0	.833	.131
99	45.4	24.4	.861	.171

(12) Ruff, Z. anorg. allgem. Chem., 206, 60 (1932).
(13) Maass and Boomer, THIS JOURNAL, 44, 1713 (1922).
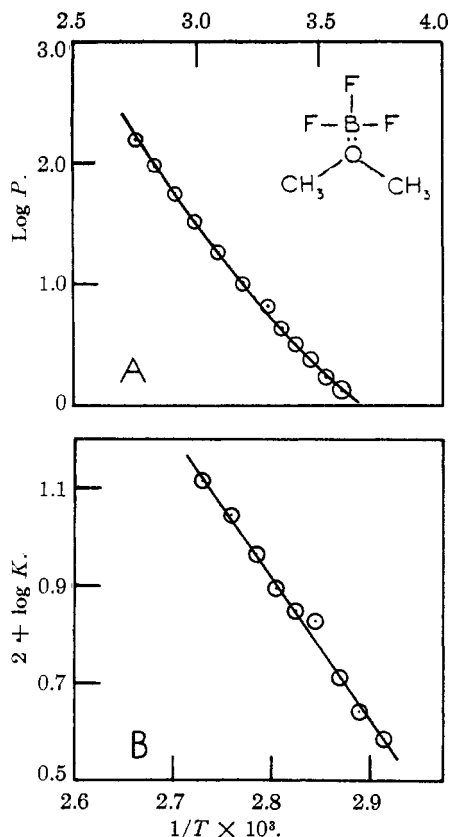(14) Gasselin, Ann. chim. phys., [7] 3, 5 (1894).

Fig. 2.—Methyl ether–boron fluoride: A, saturation pressure data; B, dissociation data.

Table II and Fig. 2-B. The data may be represented by the equation

$$\text{Log } K_p = -(2904/T) + 7.049$$

Ethyl Ether–Boron Fluoride, $(C_2H_5)_2O:BF_3$.— The addition compound, ethyl ether–boron fluoride, was prepared by the reaction of 28.0 cc. of boron fluoride and 28.3 cc. of ethyl ether (p = 186.1 mm. at 0°)[15] at low temperatures. The slight excess of ethyl ether was pumped out of the flask after the compound had warmed up to room temperature. The product was a white solid which melted to a colorless liquid at -50 to $-52°$. The saturation pressure data of the complex are given in Table III and represented graphically in Fig. 3-A.

TABLE III

SATURATION PRESSURES OF ETHYL ETHER–BORON FLUORIDE

Temp., °C.	0	5	10	20	30	40
Pressure, mm.	0.4	0.7	1.0	1.9	3.8	7.8
Temp., °C.	50	60	70	79	91	98.5
Pressure, mm.	15.2	28.2	50.1	83.3	148.8	187.1

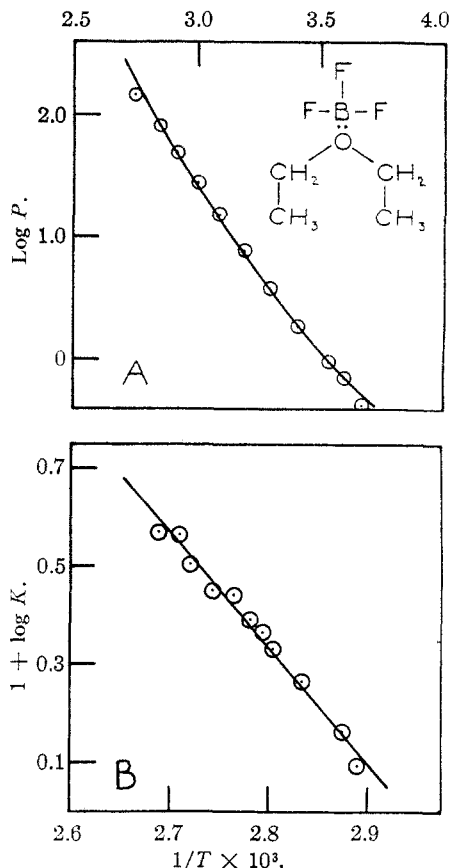(15) Taylor and Smith, THIS JOURNAL, 44, 2457 (1922).

Fig. 3.—Ethyl ether–boron fluoride: A, saturation pressure data; B, dissociation data.

The "boiling point" of the complex has been previously reported as 123–125°,[14] and as 125–126°.[16] Extrapolation of the saturation pressure curve to 760 mm. gives 124° for the "boiling point."

The dissociation of the complex was studied over a range of temperatures in the manner pre-

TABLE IV

DISSOCIATION PRESSURES OF DIETHYL ETHER–BORON FLUORIDE

Temp., °C.	Pressure observed, mm.	Pressure calculated, mm.	Degree of dissociation, α	Dissociation constant K(atm.)
73	41.6	22.7	0.833	0.124
75	42.2	22.8	.851	.146
80	43.3	23.1	.874	.184
83.5	44.1	23.4	.885	.215
85	44.5	23.5	.894	.233
86.5	44.8	23.6	.898	.246
88.5	45.2	23.7	.907	.276
91.5	45.6	23.9	.908	.282
94.5	46.2	24.1	.917	.321
96	46.6	24.2	.926	.369
99	47.0	24.4	.926	.372

(16) Hennion, Hinton and Nieuwland, THIS JOURNAL, 55, 2858 (1933).

viously described; the sample used was prepared from 5.80 cc. of ethyl ether and 5.83 cc. of boron fluoride. The results of this study are summarized in Table IV and Fig. 3-B. The data may be expressed by the equation

$$\text{Log } K_P = -(2384/T) + 6.013$$

Isopropyl Ether–Boron Fluoride, $(i\text{-}C_3H_7)_2O$: BF_3.—A commercial sample of isopropyl ether was purified by distillation through a 16-plate column. The fraction boiling at 68° under 751 mm. with $n^{20}D$ 1.3682 was used. The addition compound, isopropyl ether–boron fluoride, was prepared by condensing together (in the high temperature bulb) 31.0 cc. of boron fluoride and 31.0 cc. of isopropyl ether at the temperature of liquid nitrogen. The addition compound is a white solid at room temperature; its melting point is above 68°, but quite indefinite, apparently because of rapid decomposition of the complex at these temperatures.[17] This instability was also evidenced by its behavior during preliminary studies of its saturation pressures. At temperatures up to 45–50°, the complex did not undergo any apparent change. Above 50°, however, a slow, irreversible change of some sort occurred, for the pressure began to increase slowly, although the temperature was maintained constant. At about 68°, decomposition was so rapid that within a few minutes, the pressure rose to 180 mm.—about twice 97.8 mm., the value at 61°. After reaching this maximum value, the pressure dropped, rapidly at first, then more slowly. By working fast, and using freshly prepared samples of the complex, it was found possible to obtain reproducible values of the saturation pressures at temperatures up to 61°. The data are listed in Table V and are represented graphically in Fig. 4-A.

TABLE V

SATURATION PRESSURES OF ISOPROPYL ETHER–BORON FLUORIDE

Temp., ° C.	23	30	40	50	61
Pressure, mm.	6.4	10.1	20.6	42.5	97.8

Because of this instability of the complex its dissociation could be studied only over a relatively

(17) This decomposition was studied, but no definite conclusion was reached as to the reactions involved. It is probable that the first step is the splitting of the ether with the formation of isopropyl fluoride and isopropoxy boron fluoride, a reaction similar to the well-known reactions of boron chloride and boron bromide with ethers [Wiberg and Sütterlin, Z. anorg. allgem. Chem., 202, 22 (1931); Benton and Dillon, THIS JOURNAL, 64, 1128 (1942)]. The isopropyl fluoride then probably reacts with the boron fluoride present [Burwell and Archer, ibid., 64, 1033 (1942)], forming polymeric materials of low volatility.

short temperature range. Boron fluoride, 3.10 cc., was condensed with 3.10 cc. of isopropyl ether in the high temperature bulb in the usual manner. (It was necessary to work with a small sample in order to volatilize completely the material at a temperature where the rate of decomposition was comparatively slow.) The small size of the sample and the necessity for making rapid measurements reduce the accuracy of the data. However, they clearly indicate that the complex is highly dissociated. The results of the dissociation studies are listed in Table VI and shown graphically in Fig. 4-B. Because of the low accuracy and short temperature range, no attempt has been made to draw a line through the points on the graph (4-B).

TABLE VI

DISSOCIATION PRESSURES OF ISOPROPYL ETHER–BORON FLUORIDE

Temp., °C.	Pressure observed, mm.	Pressure calculated, mm.	Degree of dissociation, α	Dissociation constant, K(atm.)
42	20.1	11.0	0.827	0.057
44	20.5	11.0	.864	.079
46.2	20.8	11.1	.874	.089
46.5	20.9	11.1	.883	.097
51.5	21.4	11.3	.894	.112

Tetrahydrofuran–Boron Fluoride, $C_4H_8O:BF_3$. —Tetrahydrofuran was prepared by the decarboxylation of 2-furancarboxylic acid[18] followed by reduction of the resulting furan.[19] The product was distilled through a fractionating column with a rated efficiency of 16 theoretical plates, and a middle fraction (b. p. 65° at 747 mm.; $n^{20}D$ 1.4049) was taken for use in this investigation. The addition compound, tetrahydrofuran–boron fluoride, was prepared by the reaction of 35.0 cc. of tetrahydrofuran with 35.0 cc. of boron fluoride at the temperature of liquid nitrogen. The product was a white solid which melted to a colorless liquid at 8–10°. The saturation pressure data of the complex are given in Table VII and Fig. 5-A.

TABLE VII

SATURATION PRESSURES OF TETRAHYDROFURAN–BORON FLUORIDE

Temp., ° C.	39.5	58	68	79	88	98.5
Pressure, mm.	1.0	2.3	4.0	7.3	12.0	20.7

The dissociation of the complex was studied over a range of temperatures in the manner previously described, using a sample prepared from 2.46 cc. of tetrahydrofuran and 2.49 cc. of boron fluoride. The results are summarized in Table

(18) "Organic Syntheses," Coll. Vol. I, 269 (1929).
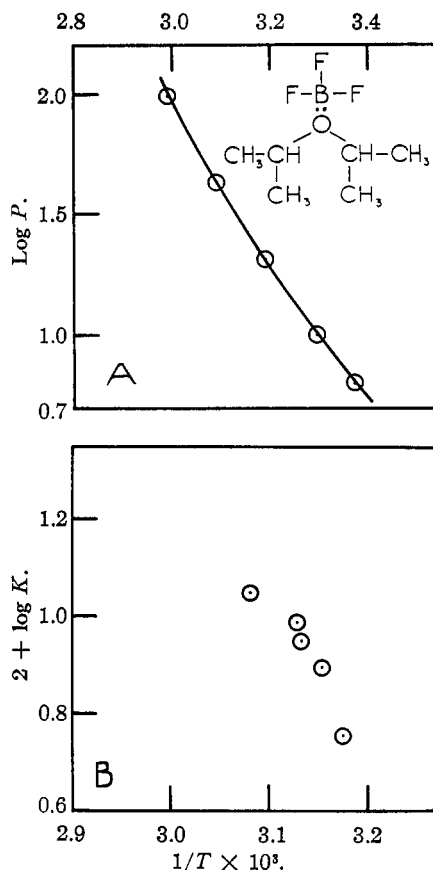(19) "Organic Syntheses," 16, 77 (1936).

Fig. 4.—Isopropyl ether–boron fluoride: A, saturation pressure data; B, dissociation data.

VIII and in Fig. 5-B. The data are expressed by the equation

$$\text{Log } K_P = (-2918/T) + 5.882$$

TABLE VIII

DISSOCIATION PRESSURES OF TETRAHYDROFURAN–BORON FLUORIDE

Temp., °C.	Pressure observed, mm.	Pressure calculated, mm.	Degree of dissociation, α	Dissociation constant, K(atm.)
94.5	15.7	10.2	0.539	0.0079
97	16.1	10.2	.578	.0106
99	16.3	10.3	.583	.0110
104	17.1	10.4	.644	.0159
108	17.4	10.5	.657	.0174
110	17.6	10.6	.660	.0178
113	18.0	10.7	.682	.0206
117	18.5	10.8	.713	.0252
123	19.1	11.0	.736	.0297

Discussion

It is a generally accepted postulate of modern electronic theories of organic chemistry that the substitution of an alkyl group for hydrogen in a molecule produces an electronic displacement away from the substituent.[20] The increase in
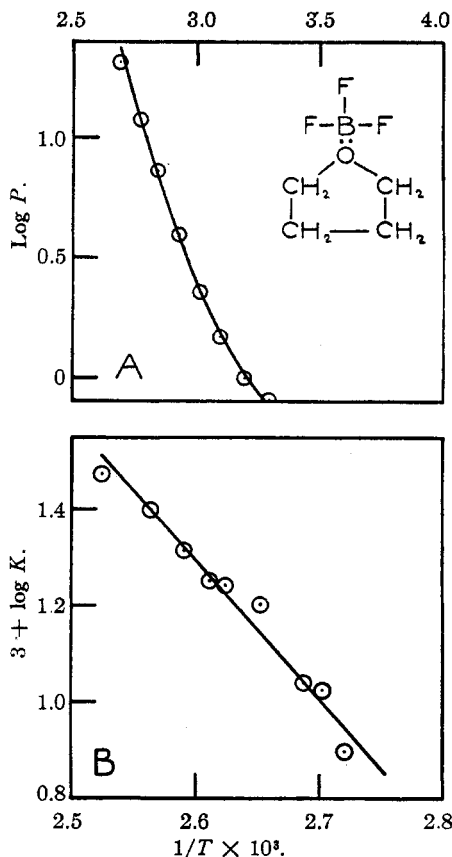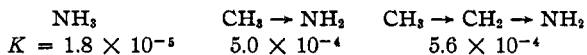
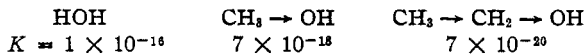(20) Ingold, *Chem. Revs.*, 15, 225 (1934).

Fig. 5.—Tetrahydrofuran–boron fluoride: A, saturation pressure data; B, dissociation data.

basicity noted in the series[21] ammonia, methylamine and ethylamine is thus explained.

$$\begin{array}{ccc} NH_3 & CH_3 \rightarrow NH_2 & CH_3 \rightarrow CH_2 \rightarrow NH_2 \\ K = 1.8 \times 10^{-5} & 5.0 \times 10^{-4} & 5.6 \times 10^{-4} \end{array}$$

The decrease in acidity in the series water,[21] methyl alcohol[22] and ethyl alcohol[23] is similarly interpreted.

$$\begin{array}{ccc} HOH & CH_3 \rightarrow OH & CH_3 \rightarrow CH_2 \rightarrow OH \\ K = 1 \times 10^{-16} & 7 \times 10^{-18} & 7 \times 10^{-20} \end{array}$$

It would, therefore, be predicted that ethyl ether should be a somewhat stronger base than methyl ether. However, if boron fluoride is used as the reference acid, the opposite is true. Under comparable conditions ethyl ether–boron fluoride is more highly dissociated than the corresponding methyl ether complex (Table IX).

It is suggested that this inversion is due to steric strains which are more important in the

(21) "Handbook of Chemistry and Physics," 25th ed., Chemical Rubber Company, Cleveland, Ohio, 1941, p. 1341.
(22) Faurholt, Z. physik. Chem., **126**, 103 (1927).
(23) Danner. This Journal, **44**, 2841 (1922).

TABLE IX

SUMMARY OF DISSOCIATION DATA FOR ETHERATES OF BORON FLUORIDE

Compound	K_{100}	K_{50}	ΔF_{100}	ΔF_{50}	ΔH	ΔS
Methyl ether–boron fluoride	0.184	0.011	1250	2900	13,300	32.3
Ethyl ether–boron fluoride	.420	.043	640	2020	10,900	27.5
Isopropyl ether–boron fluoride	..	.0115	..	1340	..	..
Tetrahydrofuran–boron fluoride	.0011	.0007	3310	4660	13,400	27.1

ethyl ether complex than in the corresponding methyl ether derivative. This conclusion is based on the following considerations. Three possible configurations of the ethyl ether molecule are shown in Fig. 6-B, D, F. The last of these may be immediately discarded because of the tremendous strains involved—the distance between the two methyl groups is only 1.7 Å. whereas the van der Waals radius of each methyl group is approximately 2.0 Å. It is more difficult to decide be-
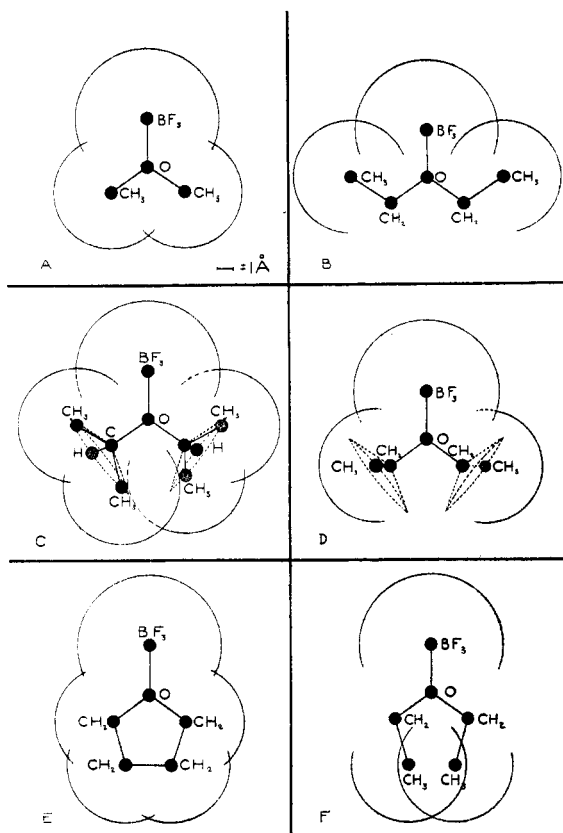

Fig. 6.—Molecular models: A, methyl ether–boron fluoride; B, D, F, ethyl ether–boron fluoride; C, isopropyl ether–boron fluoride; E, tetrahydrofuran–boron fluoride. These models are constructed using the bond distances and van der Waals radii given by Pauling.[3] The van der Waals radii are reduced somewhat (25%) to permit clearer visualization of the relative steric strains.

tween the other two possibilities (Fig. 6-B, D), but there are good reasons to believe that the arrangement shown in Fig. 6-B is the normal configuration of the ethyl ether molecule.[24]

The addition of boron fluoride to an ethyl ether molecule with this configuration must be markedly hindered as a result of the position of the end methyl groups and the size of the boron fluoride molecule (Fig. 6-B). In all probability, the addition of the boron fluoride group to the oxygen atom is accompanied by a rearrangement of the ethyl ether molecule into a configuration of somewhat higher energy, such as is shown in Fig. 6-D. As a result, the stability of the ethyl ether complex with respect to dissociation into its components is lowered relative to the corresponding methyl ether complex (Fig. 6-A).

The argument may be extended to the isopropyl ether–boron fluoride complex (a possible configuration for which is shown in Fig. 6-C), leading to the conclusion that the dissociation of this complex is also favored by the steric effects. Of the three ethers, isopropyl ether is the weakest base (Table IX), although from the inductive effect of the alkyl groups, it would have been predicted to be the strongest.

In order to test the hypothesis, the study of the dissociation of tetrahydrofuran–boron fluoride was undertaken. On the basis of the factors com-

(24) Stuart, op. cit., pp. 101–102, 236; Phys. Rev., **38**, 1372 (1931); Z. Physik, **63**, 533 (1930). Stuart bases his conclusion upon evidence from dipole moment studies, upon his investigations of the Kerr constant, and upon considerations of atomic dimensions and bond angles.

monly believed to control base strength, it would be predicted that this cyclic ether would be approximately equal in strength to ethyl ether. If steric strains play the important role ascribed to them in this publication in altering the stability of addition compounds, it follows that the base strength of this cyclic ether should be markedly greater than that of ethyl ether, since the rigidity of the five-membered ring greatly reduces the possibility of steric strains (Fig. 6-E). The fact that tetrahydrofuran–boron fluoride is by far the most stable of the etherates studied (Table IX) lends considerable support to the hypothesis of steric strain.

Summary

1. The boron fluoride addition compounds with methyl ether, ethyl ether, isopropyl ether and tetrahydrofuran have been prepared and characterized.

2. The dissociation of these compounds ($R_2O : BF_3 \rightleftarrows R_2O + BF_3$) was studied over a range of temperatures; and ΔH, ΔF and ΔS for the reaction were obtained.

3. The basic strength of the ethers decreases in the order: tetrahydrofuran, methyl ether, ethyl ether, isopropyl ether. This order is inexplicable on the basis of the factors generally believed to control base strength. The anomalies may be accounted for by taking into consideration the probable steric strains resulting from spatial limitations within the respective molecules.

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Studies in Stereochemistry. III. The Preparation of d-1-Deutero-2-methylbutane and the Study of Its Optical Rotation

BY HERBERT C. BROWN AND CORNELIUS GROOT[1]

The discovery of isotopes has brought about far-reaching changes in the prevalent concepts and has opened up a wide variety of problems for investigation. One of these which is of considerable importance to stereochemistry has not yet been conclusively solved, in spite of numerous attempts. The point at issue is whether a substance

(1) This paper is taken from a dissertation submitted by Cornelius Groot to the Faculty of the Division of the Physical Sciences of the University of Chicago, in partial fulfillment of the requirements for the degree of Master of Science.

such as $R'—\overset{\displaystyle R_1}{\underset{\displaystyle R_2}{C}}—R''$, in which the two atoms or groups R' and R'' differ only in their isotopic composition, exhibits optical activity. At the present time, all attacks upon the problem have been restricted to the use of hydrogen and deuterium as the isotopic substituents. These two isotopes differ much more than others in their chemical and physical properties; moreover, until