Experimental

Only typical syntheses are described to illustrate the general methods employed. Yield, melting point and analytical data for all the compounds prepared are summarized in Table III.

Method 1a—Two Solvent Phases. Bis-(methylamino)-hexachloro-tetraphosphonitrile.—11.59 g. (0.025 mole) of tetrameric phosphonitrilic chloride[20] was dissolved in 400 ml. of diethyl ether in a flask fitted with a stirrer and two burets. One buret contained a solution of 3.38 g. (0.05 mole) of monomethylamine hydrochloride in 100 ml. of water; the other contained a solution of 5.61 g. (0.1 mole) of potassium hydroxide in 100 ml. of water. A few drops of brom thymol blue were added to the ether solution, and the two aqueous solutions then were added to the vigorously stirred ether solution in such fashion that the reaction medium remained at the neutral point. Addition of the reagents was complete in 1 hr. The aqueous phase containing potassium chloride and hydrolysis products was removed. The ether layer was decolorized with activated charcoal, dried over calcium chloride and evaporated. The oily residue remaining was extracted with boiling petroleum ether and the crude bis-(methylamino)-hexachlorotetraphosphonitrile remaining was purified by repeated recrystallization from petroleum ether.

Method 1b—Two Solvent Phases. Bis-(anilino)-hexachloro-tetraphosphonitrile.—A solution of 46.36 g. (0.1 mole) of tetrameric phosphonitrilic chloride in 400 ml. of diethyl ether. to which *ca.* 400 ml. of water had been added, was stirred vigorously, and a solution of 37.25 g. (0.4 mole) of aniline in 100 ml. of ether was added over a period of 1 hr. Stirring then was continued for an additional hour. The ether layer next was separated and treated as outlined above. The product was purified by repeated recrystallization from *n*-heptane.

Method 2—Anhydrous Media. Bis-(N-methylanilino)-hexachloro-tetraphosphonitrile.—46.36 g. (0.1 mole) of tetrameric phosphonitrilic chloride was dissolved in 1200 ml. of anhydrous benzene. The solution was refluxed gently while 44.26 g. (0.4 mole) of N-methylaniline, diluted to double its volume with benzene, was added over a period of 3 to 4 hr. Refluxing was continued for an additional 10 hr. Precipitated amine hydrochloride was removed by filtration in the absence of moisture, and the slightly colored filtrate was evaporated to dryness without regard for separating hydrochloride. The desired product was removed by extraction with petroleum ether and purified by recrystallization from a 1:3 mixture of benzene and petroleum ether.

Instrumental Studies.—Infrared spectra were measured with a Perkin-Elmer spectrometer, Model 21, using a sodium chloride prism. The nuclear magnetic resonance spectra of phosphorus-31 were measured with a Varian Model V-4300B instrument, employing a Varian magnet Model V-4012-HR, with a 16.2 mc. radiofrequency oscillator and a field of 9395 gauss. Microanalyses for phosphorus and chlorine were made by the Clark Microanalytical Laboratory, Urbana, Illinois.

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(20) Obtained from Albright and Wilson Mfg. Ltd., Oldhury, Birmingham, England, and purified by repeated distillation in vacuum (12 mm. (188°)); m.p. 124°.

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN, ANN ARBOR, MICHIGAN]

The Boron Trifluoride Addition Compounds of Dimethyl Ether and Diethyl Ether[1,2]

BY DONALD E. MCLAUGHLIN[3] AND MILTON TAMRES

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An apparatus is described which permits convenient, rapid, and constant temperature control over a wide range of temperature in manometric studies. This is achieved by placing the reaction vessel in the vapor of a pure, boiling liquid whose boiling point can be changed rapidly to a desired temperature by varying the pressure on the liquid. As a check on the apparatus, the boron trifluoride addition compounds of dimethyl ether and diethyl ether were studied and the results are compared with those reported by Brown and Adams.[4] The agreement between the two studies is good. Somewhat closer agreement is obtained by modifying an assumption made by Brown and Adams in their investigation.

Introduction

The manometric investigation of interacting gaseous species is a method which is widely used to determine thermodynamic data for the formation of molecular addition compounds. The usual practice in such an investigation is to surround the manometric unit with a liquid bath, such as mineral oil, in order to control the temperature of the system. Since this method of temperature control is slow and somewhat inconvenient, a thermostat and manostat unit was designed which used the vapor of a pure boiling liquid for temperature regulation. With this unit a range of temperatures could be obtained by controlling the pressure upon the boiling liquid.

The addition compounds of boron trifluoride with dimethyl ether and diethyl ether were chosen to check the correct functioning of the apparatus. since thermodynamic data for the gas phase dissociation of these two addition compounds had been reported in the literature.[4,5]

An added reason for the choice of dimethyl ether:boron trifluoride for study was to attempt to clarify a somewhat controversial point regarding its stability. Analysis of electron diffraction data[6] for this addition compound, which was based on a relatively large extent of dissociation,[5] was ques-

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[1] Presented before the Division of Physical and Inorganic Chemistry at the 133rd Meeting of the American Chemical Society. San Francisco. California, April, 1958.

[2] Taken in part from the Ph.D. thesis of Donald E. McLaughlin, University of Michigan. June. 1959.

[3] Department of Chemistry, Augustana College. Rock Island, Illinois.

[4] H. C. Brown and R. M. Adams, THIS JOURNAL, **64**, 2557 (1942).

[5] A. W. Laubengayer and G. R. Findlay, *ibid.*, **65**, 884 (1943).

[6] S. H. Bauer. G. R. Findlay and A. W. Laubengayer, *ibid.*, **65**, 889 (1943).

tioned[7] and subsequently reinterpreted based upon a smaller extent of dissociation.[8] An independent determination of the stability of this addition compound seemed desirable.

Experimental

Materials.—Boron trifluoride from the Matheson Company, Inc., was purified by the method described by Brown and Johannesen.[9] The vapor pressure observed for the purified material was 157.5 mm. at −119.3 and 306.2 mm. at −111.8°. These results agree well with those calculated from the vapor pressure equation for boron trifluoride given by Pohland and Harlos.[10]

Dimethyl ether was obtained in a cylinder from the Matheson Company, Inc., dried over calcium hydride and fractionated several times in the vacuum line (vapor pressure 96.5 mm. at −63.5°).

Analytical reagent grade Mallinckrodt Chemical Works diethyl ether was dried over calcium hydride and fractionated in a short, helices packed column (b.p. 32.9° uncorr.; lit.[11] 34.1°).

The purity of the ethers was checked by vapor phase chromatography prior to their introduction into the vacuum line. Each chromatogram indicated the presence of only a single species, any impurities being present to less than 0.01%.

Apparatus.—The general features of the apparatus were as follows: The manometric unit consisted of a reaction vessel with attached mercury manometer, using a large bore tube (12 mm. diameter) to minimize the correction which is necessary when the meniscus height in the two arms is not equal.[12] A mercury float valve between the manometer and the vacuum line made it unnecessary to correct pressure readings at the higher temperatures for the vapor pressure of mercury in the reaction vessel. An insulated jacket surrounded this assembly, and to this jacket a flask containing the boiling liquid was attached. By means of the manostat assembly, any desired constant pressure could be maintained inside the jacket for long periods of time.

The operation of the complete apparatus when making dissociation measurements is described: A suitable amount of one species was condensed into the evacuated reaction vessel by cooling with liquid nitrogen. The vapor thermostat was placed in operation, and sufficient time was allowed for thermal equilibrium. Ordinarily, the pressure of the single species was recorded at three temperatures over a twenty to thirty degree range and the results were averaged. Pressure readings were corrected for the density of mercury, for capillarity, and to a constant reference volume. This measured single species was transferred quantitatively, using liquid nitrogen, to a storage place in the vacuum line, after which an approximately equivalent amount of a second species was measured. The two then were condensed together in the reaction vessel, and dissociation pressures were determined at five degree intervals over approximately a thirty-five degree temperature range. These were taken in random fashion to avoid certain systematic errors. The results at several temperatures were rechecked at the end of a run in order to verify the absence of any secondary reaction during the course of the run.

Vapor pressures (or saturation pressures) of the addition compounds at temperatures above that of the room were measured in the dissociation apparatus. This has the disadvantage that, since the volume of the reaction bulb is so large, it is necessary to take quite large amounts of sample in order to get good saturation pressure data. Log P *versus* $1/T$ plots exhibited considerable curvature when the sample size was too small. Vapor pressures of substances at temperatures below room temperature were measured in a small volume manometer.

The melting points of the addition compounds were determined in one of two ways. Substances melting at higher than room temperature were condensed into capillaries and sealed off under vacuum, and the melting points were determined visually in a liquid bath in the usual way. For substances melting considerably below room temperature, the Stock-type falling rod apparatus[13] was used.

Results

Dimethyl Ether : Boron Trifluoride.—Saturation pressure data for the colorless liquid addition compound are listed in Table I. These data are in fair agreement with those reported by Brown and Adams.[4] Also the melting point of the white solid, − 12.0 to − 11.8°, is very nearly the same as that given in the literature.[14]

TABLE I

SATURATION PRESSURES OF DIMETHYL ETHER:BORON TRIFLUORIDE

Saturation pressure equation (liquid): $\log P = \frac{-2775}{T} + 9.806$

Temp. (°C.)	Pressure (mm.)	Temp. (°C.)	Pressure (mm.)
38.1	7.85	59.9	30.04
42.2	10.27	64.6	38.84
48.2	14.87	70.1	53.16
54.7	22.09	73.0	61.96

The dissociation constant for the addition compound was calculated assuming interaction in 1:1 ratio only,[15] and assuming ideal gas behavior. Numerical data in the temperature range 60 to 95° are presented in Table II.

TABLE II

DISSOCIATION DATA FOR DIMETHYL ETHER:BORON TRIFLUORIDE

$$\log K = \frac{-2983}{T} + 7.228$$

Temp. (°C.)	Pressure (mm.)	Dissoc. const. K (atm.)
13.166 mm. BF_3 and 12.531 mm. dimethyl ether at 0°		
59.9	25.049	0.0184
65.2	26.286	.0255
69.9	27.425	.0346
74.9	28.558	.0467
79.8	29.502	.0591
84.9	30.526	.0780
89.7	31.459	.102
94.8	32.343	.131
14.205 mm. BF_3 and 14.352 mm. dimethyl ether at 0°		
65.3	28.970	0.0261
74.8	31.353	.0454
84.9	33.691	.0789
94.9	35.788	.134

Diethyl Ether:Boron Trifluoride.—The saturation pressure data for this addition compound are listed in Table III, and these data are in good agreement with those reported by Brown and Adams.[4] The white solid melts[16] to give a colorless liquid at − 54 to − 52°.

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[7] H. C. Brown and R. M. Adams, THIS JOURNAL, **65**, 2253 (1943).

[8] S. H. Bauer, G. R. Findlay and A. W. Laubengayer, *ibid.*, **67**, 339 (1945).

[9] H. C. Brown and R. B. Johannesen, *ibid.*, **72**, 2934 (1950).

[10] Von E. Pohland and W. Harlos, *Z. anorg. allgem. Chem.*, **207**, 242 (1932).

[11] A. Weissberger, Ed., "Technique of Organic Chemistry," Vol. VIII, "Organic Solvents," 2nd ed., Interscience Publishers, Inc., New York, N. Y., 1955.

[12] W. Cawood and H. S. Patterson, *Trans. Faraday Soc.*, **29**, 552 (1933).

[13] A. Stock, *Ber.*, **50**, 156 (1917).

[14] (a) −14 to −12° ref. 4; (b) −14° ref. 5.

[15] H. E. Wirth, M. J. Jackson and H. W. Griffiths, *J. Phys. Chem.*, **62**, 871 (1958), report that dimethyl ether and boron trifluoride form only the 1:1 complex.

[16] Literature values are: (a) −52 to −50° ref. 4; (b) −60.4° ref. 5; (c) −59° ref. 15; (d) −57.8 to −57.7° N. N. Greenwood, R. L. Martin and H. J. Emeleus, *J. Chem. Soc.*, 3030 (1950).

TABLE III

SATURATION PRESSURES OF DIETHYL ETHER:BORON TRIFLUORIDE

Saturation pressure equation (liquid): $\log P = \frac{-2879}{T} + 10.082$

Temp. (°C.)	Pressure (mm.)	Temp. (°C.)	Pressure (mm.)
10.0	0.80	60.0	28.00
19.5	1.75	69.9	49.60
29.8	4.08		
39.7	7.69		
50.0	15.05		

Diethyl ether and boron trifluoride form a stable addition compound of 1:3 ratio as well as the 1:1 compound, but the former decomposes upon heating to give the latter.[15] Only 1:1 interaction was considered in calculating the dissociation constant, and numerical data in the temperature range 60 to 95° are given in Table IV.

TABLE IV

DISSOCIATION DATA FOR DIETHYL ETHER:BORON TRIFLUORIDE

Temp. (°C.)	Pressure (mm.)	Dissoc. const. K (atm.)
12.944 mm. BF_3 and 12.802 mm. diethyl ether at 0° $\log K = -2607/T + 6.597$		
67.7	29.437	0.0898
69.9	29.829	.0981
72.4	30.287	.113
74.9	30.696	.128
80.1	31.540	.166
84.8	32.234	.207
89.8	32.951	.263
94.7	33.608	.319
11.452 mm. BF_3 and 10.953 mm. diethyl ether at 0°[a] $\log K = -2561/T + 6.385$		
59.9	24.290	0.0491
65.0	25.118	.0636
69.9	25.980	.0865
74.9	26.727	.101
79.9	27.369	.138
84.8	27.962	.166
90.0	28.661	.222
94.7	29.168	.260

[a] Because of experimental difficulties with mercury sticking in the manometer, this set of data is not considered as reliable as the first set given.

Discussion

The heat of dissociation of the boron trifluoride etherates was evaluated from the plot of log K *versus* $1/T$, where the best straight line through the points was determined by the method of least squares. The thermodynamic data are summarized in Table V, together with the values of Brown and Adams[4] for these two addition compounds. The results of this study for the dimethyl ether:boron trifluoride compound support the data of Brown and Adams[4] rather than those of Laubengayer and Findlay.[5]

In comparing the thermodynamic values with those of Brown and Adams, mention should be made of a difference in experimental technique which was employed in the two investigations. In the apparatus of Brown and Adams, one arm of the manometer was always open directly to the vacuum line; this was altered in subsequent models,[17,18] so that it seemed necessary to reduce all observed pressure readings by an amount equal to the vapor pressure of mercury in the reaction vessel at that temperature. In the apparatus of the present investigation, the float valve inside the thermostat and between the manometer and the vacuum line made it possible to determine experimentally whether or not this procedure is valid. Table VI shows the experimental difference in pressure readings obtained with the float valve first open and then closed at a number of temperatures. Compared with the experimental values are the values which follow from the assumption of zero pressure on the arm of the manometer open to the vacuum line.

These data show that the assumption of zero pressure on the arm open to the vacuum line is not valid. The explanation of this is probably that the heavy mercury vapor is not being pumped away from the space above the meniscus nearly as fast as it is vaporizing. The exact magnitude of this effect at a particular temperature no doubt depends to a small extent on distance from the vacuum pump, size and number of bends in the tubing, etc. The data of Table VI also show that the error due to assuming zero pressure on the arm of the manometer open to vacuum line becomes progressively greater as the temperature increases.

The results of Table VI can be used to apply a correction to the numerical dissociation data of Brown and Adams for both dimethyl ether:boron trifluoride and diethyl ether:boron trifluoride. The procedure of correcting their data using experimental results obtained on another apparatus is not entirely justifiable; but since the correction is not large, and since it should depend to only a small degree on the physical features of the individual apparatus, its application should be essentially correct. The effect of this correction on the data of Brown and Adams is shown in Table V. The correction results in an increase in the dissociation constant at all temperatures, but the correction is largest at the higher temperatures where the constant is most sensitive to changes in the pressure. Therefore, application of the correction results in a change in the slope of the log K *versus* $1/T$ line and, hence, an increase in the enthalpy term. As can be seen in Table V, the agreement in the enthalpy and entropy values is somewhat improved and the free energy change made slightly more divergent by the application of the correction.

The slightly higher values obtained in this work for the heats of dissociation of these boron trifluoride etherates produce correspondingly slightly higher results for the entropy terms. However, the increase is not sufficient to support the expectations of Shepp and Bauer.[19] These authors calculated from available and estimated spectroscopic parameters that the entropy of dissociation of dimethyl ether:boron trifluoride must have a

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(17) H. C. Brown, M. D. Taylor and M. Gerstein, THIS JOURNAL, **66**, 431 (1944).

(18) H. C. Brown and M. Gerstein, *ibid.*, **72**, 2923 (1950).

(19) A. Shepp and S. H. Bauer, *ibid.*, **76**, 265 (1954).

TABLE V

THERMODYNAMIC DISSOCIATION DATA FOR ADDITION COMPOUNDS OF DIMETHYL ETHER AND DIETHYL ETHER WITH BORON TRIFLUORIDE

	ΔH^0 (kcal./mole)	K_{100} (atm.)	ΔF^0_{100} (cal./mole)	ΔS^0 (e.u.)
This research:				
Dimethyl ether: BF_3	13.65 ± 0.2	0.172	1308 ± 20	33.1 ± 0.6
Diethyl ether: BF_3	11.93 ± 0.3	.408	665 ± 30	30.2 ± 0.8
Brown and Adams[4]:				
Dimethyl ether: BF_3	13.3	.184	1250	32.3
Diethyl ether: BF_3	10.9	.420	640	27.5
Brown and Adams with correction:				
Dimethyl ether: BF_3	14.0	.200	1194	34.3
Diethyl ether: BF_3	11.9	.464	569	30.4

TABLE VI

MERCURY VAPOR CORRECTION

Temp. (°C.)	Exp. corr. (this apparatus), mm.	Lit. vapor press. (assumption of Brown and Adams), mm.
69.6	0.01	0.05
86.1	.03	.13
95.8	.05	.22
110.0	.08	.46
120.4	.11	.76
125.0	.12	.94

lower limit of 35.7 e.u., and very probably is in the range 40 to 41 e.u. In view of the present work, their conclusion that the values for ΔS^0 of these etherates must be low by approximately 8 to 9 e.u. does not seem justified. It does not seem likely that deviations from ideal behavior could account for this large difference from the value estimated by Shepp and Bauer, especially since the deviations should be more pronounced at the lower temperatures and would give an experimental result for ΔH^0 which is high. Further spectroscopic work on these boron trifluoride etherates seems warranted.

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[CONTRIBUTION FROM THE CHEMISTRY LABORATORIES OF THE UNIVERSITY OF MICHIGAN, ANN ARBOR, MICHIGAN AND KANSAS STATE UNIVERSITY, MANHATTAN, KANSAS]

The Addition Compounds of Cyclic Ethers with Boron Trifluoride[1,2]

BY DONALD E. MCLAUGHLIN,[3] MILTON TAMRES AND SCOTT SEARLES, JR.

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The stabilities of the addition compounds of cyclic ethers with boron trifluoride were investigated by a manometric method. Ethylene oxide and trimethylene oxide polymerized in contact with boron trifluoride. Thermodynamic results for the addition compounds with tetrahydrofuran and tetrahydropyran indicate that the 5-membered ring is the better electron donor. This is attributed to a ring size effect. Nuclear magnetic resonance spectra show that the boron trifluoride has a pronounced effect in decreasing the electron shielding around the ring protons in the cyclic ethers.

Introduction

In view of the evidence for ring size effects in the weak interactions with cyclic ethers, *e.g.*, hydrogen bonding[4] and iodine complex formation,[5] it was felt of interest to see if these effects might not also be operative in a strong interaction such as with boron trifluoride. Unusual stability of the addition compound formed by boron trifluoride with the cyclic ether tetrahydrofuran in comparison with open chain ethers had been observed, but the difference was attributed to "F-strain."[6] Apart from the interest in the ring size effect, it was felt desirable to look further into the puzzling situation that the heat of formation of the addition compound with boron trifluoride was the same for tetrahydrofuran as for dimethyl ether,[6] although the dissociation constant for the former was considerably smaller.

Experimental

Materials.—The boron trifluoride used was the same as that described previously.[7]

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[1] Presented in part before the Division of Physical and Inorganic Chemistry at the 133rd Meeting of the American Chemical Society, San Francisco, California, April, 1958.

[2] Taken in part from the Ph.D. thesis of Donald E. McLaughlin, University of Michigan, June, 1959.

[3] Department of Chemistry, Augustana College, Rock Island, Illinois.

[4] S. Searles and M. Tamres, THIS JOURNAL, **73**, 3704 (1951).

[5] Sister M. Brandon Hudson, Ph.D. Thesis, University of Michigan, 1957.

[6] H. C. Brown and R. M. Adams, THIS JOURNAL, **64**, 2557 (1942).

[7] D. E. McLaughlin and M. Tamres, *ibid.*, **82**, 5618 (1960).