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.

Acknowledgment.—This research was supported in part by a grant from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of this fund. D. E. M. wishes to thank the Horace H. Rackham School of Graduate Studies of The University of Michigan for a University Fellowship. A separate grant from the Horace H. Rackham School was used to purchase equipment. The authors also wish to express their thanks to Mr. George Killich for his work in the construction of the vacuum line and the manostat unit.

[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).

Technical grade tetrahydrofuran and tetrahydropyran from the du Pont Company were purified as described elsewhere.[8] Analysis of these ethers by vapor phase chromatography indicated the absence of impurities.

Apparatus.—The constant temperature manostat reported previously[7] was employed for the vapor phase study of the addition compounds.

Proton magnetic resonance spectra were taken on a Varian High Resolution NMR Spectrometer, Model V-4300B (with fixed frequency of 40 mc.).

Results

Ethylene Oxide and Trimethylene Oxide.—Gaseous boron trifluoride was added to each of the liquid ethers at −20°. After absorbing an approximately equivalent amount of boron trifluoride in a matter of ten minutes, the mixture was allowed to warm to room temperature, whereupon both the ethylene oxide and the trimethylene oxide underwent a rapid and irreversible reaction with boron trifluoride, converting the clear liquid mixture into a gummy polymer-like material accompanied by considerable evolution of heat. No attempt was made to pursue the problem of determining the reaction products. This has been done for the ethylene oxide–boron trifluoride system.[9] At low temperatures (below − 80°) the 1:1 complex has been reported to exist.[10]

Tetrahydrofuran:Boron Trifluoride.—Unlike the smaller ring ethers, tetrahydrofuran and boron trifluoride form a stable 1:1 compound. The white solid melts to a colorless liquid between 11.7 and 12.3°, this being the same as that (12°) reported by Wirth, Jackson and Griffiths[11] and only slightly higher than the range of 8 to 10° reported by Brown and Adams.[6]

The saturation pressures of the liquid phase are presented in Table I. These data are in agreement with those of Brown and Adams,[6] except for a few points at the lower temperatures which may be due to their having a slight excess of one component in forming the 1:1 addition compound. However, the data for the dissociation constants, given in Table II, are not in good agreement. A possible explanation for the difference will be given in the Discussion section.

TABLE I

SATURATION PRESSURES OF TETRAHYDROFURAN:BORON TRIFLUORIDE

Saturation pressure equation (liquid): $\log P = \frac{-3126}{T} + 9.734$

Temp. (°C.)	Pressure (mm.)	Temp. (°C.)	Pressure (mm.)
21.3	0.13	89.9	13.33
24.3	0.17	94.9	17.44
59.9	2.28	100.0	22.71
69.8	4.21	105.0	29.38
79.8	7.57	110.0	37.78

Tetrahydropyran:Boron Trifluoride.–Tetrahydropyran also forms a stable 1:1 addition compound with boron trifluoride. The white solid melts to a colorless liquid in the range 9.5 to 10.2°. A melting point[11] of 11° and a melting point[10] of −18° have been obtained from cryoscopic studies.

TABLE II

DISSOCIATION DATA FOR TETRAHYDROFURAN:BORON TRIFLUORIDE

Temp. (°C.)	Pressure (mm.)	Dissoc. const. K (atm.)
7.645 mm. BF_3 and 7.936 mm. tetrahydrofuran at 0°		
$\log K = \frac{-3677}{T} + 8.009$		
96.3	16.675	0.0113
99.9	17.225	.0141
104.9	18.029	.0195
109.9	18.734	.0258
110.2	18.828	.0270
114.6	19.424	.0342
119.9	20.081	.0443
120.2	20.108	.0446
124.8	20.727	.0587
127.3	21.072	.0692
7.898 mm. BF_3 and 8.005 mm. tetrahydrofuran at 0°		
$\log K = \frac{-3661}{T} + 7.968$		
99.7	17.549	0.0142
104.6	18.281	.0188
110.0	19.124	.0263
115.0	19.829	.0346
119.9	20.486	.0449
125.0	21.129	.0584
129.0	21.664	.0746

TABLE III

SATURATION PRESSURES OF TETRAHYDROPYRAN:BORON TRIFLUORIDE

Saturation pressure equation (liquid): $\log P = \frac{-3183}{T} + 10.090$

Temp. (°C.)	Pressure (mm.)	Temp. (°C.)	Pressure (mm.)
50.0	1.77	80.1	11.91
60.0	3.44	84.8	15.74
64.9	4.65	89.6	20.96
70.5	6.59	95.1	28.21
74.9	8.88		

TABLE IV

DISSOCIATION DATA FOR TETRAHYDROPYRAN:BORON TRIFLUORIDE

$$\log K = \frac{-3369}{T} + 7.558$$

Temp. (°C.)	Pressure (mm.)	Dissoc. const. K (atm.)
11.105 mm. BF_3 and 11.075 mm. tetrahydropyran at 0°		
96.0	18.585	0.0268
100.1	18.907	.0336
104.6	19.333	.0434
109.8	19.729	.0562
114.4	20.135	.0747
119.8	20.486	.0986
124.5	20.718	.121
129.5	20.981	.158
10.988 mm. BF_3 and 11.394 mm. tetrahydropyran at 0°		
99.9	19.057	0.0334
100.1	19.059	.0335
110.1	19.964	.0587
119.8	20.622	.0956
129.5	21.136	.154

(8) Sister M. Brandon, O.P., M. Tamres and S. Searles, Jr., THIS JOURNAL, **82**, 2129 (1960).

(9) N. N. Greenwood, R. L. Martin and H. J. Emeleus, *J. Chem. Soc.*, 3030 (1950).

(10) J. Grimley and A. K. Holliday, *ibid.*, 1215 (1954).

(11) H. E. Wirth, M. J. Jackson and H. W. Griffiths, *J. Phys. Chem.*, **62**, 871 (1958).

TABLE V

THERMODYNAMIC DISSOCIATION DATA FOR ADDITION COMPOUNDS OF TETRAHYDROFURAN AND TETRAHYDROPYRAN WITH BORON TRIFLUORIDE

	ΔH^0 (kcal./mole)	K_{100} (atm.)	ΔF^0_{100} (cal./mole)	ΔS^0 (e.u.)
This research:				
Tetrahydrofuran:BF_3	16.80 ± 0.2	0.0144	3145 ± 20	36.6 ± 0.6
Tetrahydropyran:BF_3	15.42 ± 0.2	.0339	2510 ± 20	34.6 ± 0.6
Brown and Adams:[6]				
Tetrahydrofuran:BF_3	13.4	.011	3310	27.1
Brown and Adams with correction:				
Tetrahydrofuran:BF_3	16.0	.014	3192	34.3

Saturation pressure data for this addition compound are given in Table III. The equation for saturation pressure determined in this study is different from that of Grimley and Holliday,[10] although the extrapolated "boiling points" are only 6° apart (168° in this study, 162° in theirs). Data for the dissociation constants are listed in Table IV.

Discussion

An examination of the thermodynamic values of Table V for tetrahydrofuran:boron trifluoride shows poor agreement between the results of this research and those of Brown and Adams. As discussed previously,[7] the assumption of zero pressure on the arm of the manometer open to the vacuum line leads to error, particularly at the higher temperatures. Its effect on the dissociation constants and, hence, on the slope of the log K *versus* $1/T$ plot is much more serious for tetrahydrofuran:boron trifluoride than for dimethyl ether:boron trifluoride or for diethyl ether:boron trifluoride (which were studied at a lower temperature range). In Figure 1, the log K *versus* $1/T$ plot of the data of this research is compared with the uncorrected and corrected[12] data of Brown and Adams. It may be seen from Figure 1 and also from the thermodynamic values of Table V that the correction brings the two studies into appreciably better agreement.

The value in ΔH^0, higher by 3.4 kcal./mole, obtained in this work results in a correspondingly higher value for ΔS^0 by about 10 e.u. The increase in ΔS^0 is in accord with the expectations of Shepp and Bauer.[13] However, this cannot be taken as support for the general validity of their entropy estimates since their conclusions did not agree with the experimental results for the boron trifluoride addition compounds with dimethyl ether and diethyl ether.[7]

There is an enormous difference in the result for ΔH^0 obtained in this study for the tetrahydropyran:boron trifluoride system and that reported by Grimley and Holliday[10] (38 kcal./mole).[14] By comparing this large value to that reported by Brown and Adams[6] for tetrahydrofuran:boron trifluoride and also by using a qualitative means to estimate relative stabilities of cyclic ether:boron trichloride systems,[15] Grimley and Holliday proposed a tentative order of stability which led to the conclusion that stability varied directly with ring size.

An entirely opposite conclusion would have to be drawn from this study. A comparison of the thermodynamic values for ΔH^0 of Table V for tetrahydrofuran:boron trifluoride and tetrahydropyran:boron trifluoride reveals that the 6-membered ring ether forms a weaker complex with boron trifluoride than does the 5-membered ring ether. This is in agreement with the studies reported on hydrogen bonding[4] and iodine complex formation[5] of the cyclic ethers, and suggests that the ring size effect is operative in strong interactions as well as weak.

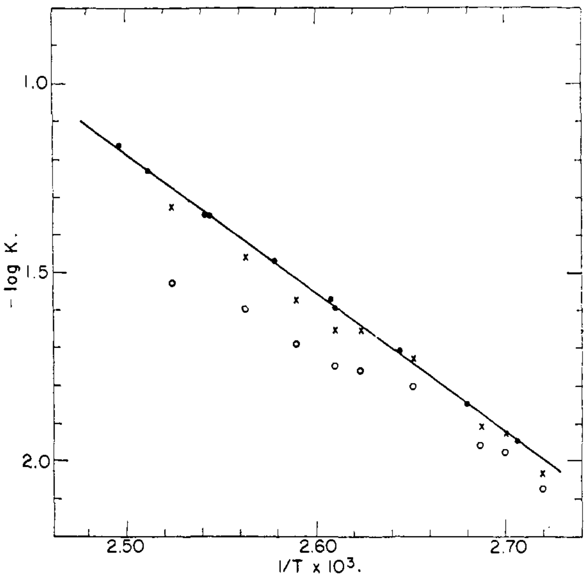

Fig. 1.—Log K *vs.* $1/T$ for tetrahydrofuran:boron trifluoride: ●, this research; ○, Brown and Adams[6]; ×, Brown and Adams with experimental correction.

It seems preferable not to invoke "F-strain" to explain the relative electron donor ability of the 5- and 6-membered ring cyclic ethers toward boron trifluoride since the same order of basicity was observed in the studies of iodine complex formation and of hydrogen bonding where "F-strain" was shown not to be applicable. If "F-strain" were of very great importance, it would be surprising that the steric requirements in complex formation of the ethers with the two reference acids, iodine and boron trifluoride, would be similar. Yet, for the limited number of ethers for which common data are available, namely, diethyl ether, tetrahydrofuran and tetrahydropyran, the enthalpy data are related linearly as is shown in Fig. 2.

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[12] Correction based upon the data of Table VI of ref. 7, subject to the limitations discussed in that paper.

[13] A. Shepp and S. H. Bauer, THIS JOURNAL, **76**, 265 (1954).

[14] This result is highly unlikely since it would result in much too large a value for ΔS^0. The authors cautioned that their ΔH^0 determination was based on limited data.

[15] J. Grimley and A. K. Holliday, *J. Chem. Soc.*, 1212 (1954).

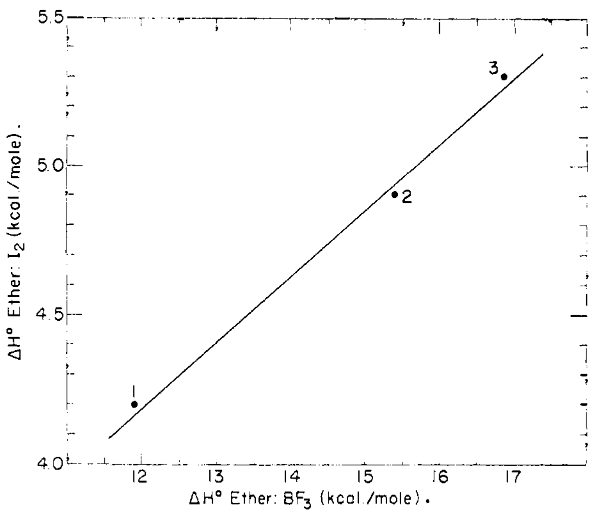

Fig. 2.—$\Delta H°$ for ether–iodine complexes *vs.* $\Delta H°$ for ether–boron trifluoride addition compounds: 1, diethyl ether; 2, tetrahydropyran; 3, tetrahydrofuran.

As pointed out previously from hydrogen bonding,[4] iodine complex formation[5] and proton magnetic resonance[16] studies, an alternate explanation for the relative order of basicity is that the electron donor ability of the oxygen atom in each of these ethers is intrinsically different. This may occur because unusual geometrical requirements, such as arise in ring formation, alter the orbital hybridization of the atoms and, hence, their electron distribution which in turn affects the properties of the molecule.

In complexation with dinitrogen tetroxide, Sisler and co-workers[17] have observed the same order of donor ability for tetrahydrofuran, tetrahydropyran and diethyl ether as that found for the boron trifluoride complexes, namely, tetrahydrofuran> tetrahydropyran> diethyl ether. Although "F-strain" was first offered as a possible explanation, later results by Sisler and co-workers on the dinitrogen tetroxide complexes of 2-methyltetrahydrofuran[18] and 2,5-dimethyltetrahydrofuran[19] do not support that explanation. Both 2-methyltetrahydrofuran and 2,5-dimethyltetrahydrofuran were found to be better donors toward dinitrogen tetroxide than was tetrahydrofuran itself. The authors concluded that the steric effect of the alpha methyl groups could not be very large. They noted further that whereas steric factors could not explain their data, the results were in agreement with those expected on the basis of the ring size effect.

Recently, data have been presented by Schaeffer and co-workers[20] on the thermodynamic stabilities of the etherates of lithium borohydride with dimethyl ether, diethyl ether and tetrahydrofuran. These authors observed an order of donor ability of tetrahydrofuran> dimethyl ether> diethyl ether. Although their interpretation of the data was based on steric considerations, the concept of change in orbital hybridization could also be used to explain the results. Similar comment can be made for the comparable studies made on the ether–diborane addition compounds.[21]

Proton Magnetic Resonance.—It is known from spectroscopic studies of addition compounds that the coördination of the acid species with the base brings about changes in certain frequencies originally associated with the free base as well as giving rise to certain new frequencies attributable to the complex itself. The perturbation of the electronic structure of the base ought to be indicated also from a comparison of the proton magnetic resonance spectrum of the free base with that of the complex. It was thought that a study of the proton magnetic resonance spectra of the boron trifluoride complexes of the unsubstituted cyclic ethers might also yield additional information on ring size effects in cyclic systems. Unfortunately, the rapid irreversible reaction of boron trifluoride with ethylene oxide and trimethylene oxide did not permit an NMR study. However, samples of the 1:1 addition compound of boron trifluoride with tetrahydrofuran and tetrahydropyran were easily prepared in the vacuum line, condensed into NMR tubes and sealed off under vacuum.

Proton magnetic resonance chemical shifts[22] for tetrahydrofuran, tetrahydrofuran:boron trifluoride, tetrahydropyran and tetrahydropyran: boron trifluoride are shown in Table VI, together with values for approximately 50 mole % mixtures of chloroform with tetrahydrofuran and tetrahydropyran.

TABLE VI

PROTON MAGNETIC RESONANCE CHEMICAL SHIFTS OF CYCLIC ETHER COMPLEXES

System	δ Value[a,b] ± 0.01	
	α-CH₂	β-CH₂
Tetrahydrofuran (pure)	−0.14	−0.33
Tetrahydrofuran (58.9 mole % in $CHCl_3$)	− .12	− .31
Tetrahydrofuran: BF_3	− .06	− .28
	α-CH₂	β,γ-CH₂
Tetrahydropyran (pure)	−0.15	−0.35
Tetrahydropyran (54.3 mole % in $CHCl_3$)	− .13	− .33
Tetrahydropyran: BF_3	− .07	− .32

[a] Water reference. [b] Terminology is that of ref. 22.

The proton magnetic resonance spectrum of pure tetrahydrofuran contains two bands of equal intensity at $\delta = -0.14$ and $\delta = -0.33$ assigned to protons on the alpha and beta carbon atoms, respectively.[23] The spectrum of the tetrahydrofuran:boron trifluoride addition compound also shows just two bands similar in appearance to those of the pure ether but shifted in position in the di-

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(16) H. S. Gutowsky, R. L. Rutledge, M. Tamres and S. Searles, THIS JOURNAL, **76**, 4242 (1954).

(17) B. Rubin, H. H. Sisler and H. Schechter, *ibid.*, **74**, 877 (1952).

(18) J. G. Whanger and H. H. Sisler, *ibid.*, **75**, 5188 (1953).

(19) H. H. Sisler and P. E. Perkins, *ibid.*, **78**, 1135 (1956).

(20) (a) G. W. Schaeffer and T. L. Kolski, Paper presented before the Division of Physical and Inorganic Chemistry, New York City, N. Y., Sept., 1957, Abstracts p. 95; (b) G. W. Schaeffer, T. L. Kolski, and L. D. Ekstedt, THIS JOURNAL, **79**, 5912 (1957); (c) T. L. Kolski, H. B. Moore, L. E. Roth, K. J. Martin and G. W. Schaeffer, *ibid.*, **80**, 549 (1958).

(21) (a) B. Rice, J. Livasy and G. W. Schaeffer, *ibid.*, **77**, 2750 (1955); (b) B. Rice and H. S. Uchida, *J. Phys. Chem.*, **59**, 650 (1955); (c) H. E. Wirth, F. E. Massoth and D. X. Gilbert, *ibid.*, **62**, 870 (1958).

(22) The terminology used here is that given by H. S. Gutowsky, D. W. McCall, B. R. McGarvey and L. H. Meyer, *J. Chem. Phys.*, **19**, 1328 (1951).

(23) These shifts are slightly different from those reported in ref. 16.

rection of decreasing field, resulting in $\delta = -0.06$ and $\delta = -0.28$ for the protons of the alpha and beta carbon atoms.

The proton magnetic resonance spectrum of pure tetrahydropyran contains two peaks of intensity ratio 2:3 at $\delta = -0.15$ and $\delta = -0.35$, the first being attributed to protons of the alpha methylenes and the second to protons of the beta and gamma methylenes.[23] Again, the spectrum of the tetrahydropyran:boron trifluoride shows two peaks similar in appearance to those of the pure ether but shifted in the direction of decreasing field, and they now appear at $\delta = -0.07$ and $\delta = -0.32$.

It is clear, shown also by Diehl and Ogg,[24] that the shifts which arise from coördination can be appreciable. Coördination affects the total electronic structure of the base, making the protons of the complexed ether less shielded or more protonic than those of the uncomplexed ether. The effect of chloroform in this respect is very small,[25] which is to be expected because of the weakness of the hydrogen bond. However, in the case of the stronger binding with boron trifluoride, the protonic character of the hydrogens of the ether is markedly increased, especially for those attached to the alpha carbon atoms. The formation of the dative bond between the oxygen atom of the ether and the boron atom of the boron trifluoride results in some shift of charge in the bonds adjacent to the oxygen atom. This in turn produces a shift in the electrons binding the alpha hydrogen atom and results in the observed increase in protonic character. Apparently, the effect falls off rapidly for atoms more removed from the oxygen. The magnitude of the effect on the alpha hydrogen upon complex formation with boron trifluoride is the same for the 5- and the 6-membered rings within experimental sensitivity.

Additional evidence for the effect of complexation upon the electronic structure of the boron trifluoride addition compound comes from studies[26,27] of the fluorine magnetic resonance in liquid boron trifluoride ($\delta = 4.6$) compared with that in the boron trifluoride diethyl etherate ($\delta = 1.4$ to 2.5), where the shifts are referred to the fluorine resonance in BeF_2 as zero. The direction of the shift shows that complexation with the ether markedly increases the shielding of the fluorine atoms.

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[24] P. Diehl and R. A. Ogg, *Nature*, **180**, 1114 (1957).

[25] The shift of 0.02 units in the δ-values is at the limit of the sum of the estimated experimental errors for the technique used. However, the shift seems real and may be due due in part to solvent effects other than that of hydrogen bonding. Mr. LeRoy Johnson, of Varian Associates, obtained the following results using an audio-oscillator to match peak heights with tetramethylsilane as an internal standard (on the V-4300C High Resolution NMR Spectrometer):

System	δ-Value for CH_2's (relative to H_2O)	
Tetrahydrofuran (35.6 mole % in CCl_4)	$\alpha = 0.123$	$\beta = 0.305$
Tetrahydrofuran (34.7 mole % in $CHCl_3$)	$\alpha = .112$	$\beta = .300$
Tetrahydropyran (37.1 mole % in CCl_4)	$\alpha = .135$	$\beta + \gamma = 0.330$
Tetrahydropyran (36.9 mole % in $CHCl_3$)	$\alpha = .125$	$\beta + \gamma = .325$

These samples had been run previously in this Laboratory, and the results were in excellent agreement with the more precise data of Mr. Johnson.

[26] H. S. Gutowsky and C. J. Hoffman, *Phys. Rev.*, **80**, 110 (1950).

[27] W. C. Dickinson, *ibid.*, **81**, 717 (1951).

[CONTRIBUTION FROM THE MALLINCKRODT LABORATORY OF CHEMISTRY AT HARVARD UNIVERSITY, CAMBRIDGE, MASSACHUSETTS]

Coördination of Polymeric Organosilyl Amines. I. Reactions with Copper(II) Ion

BY RONN MINNÉ AND EUGENE G. ROCHOW

RECEIVED MARCH 12, 1960

Anhydrous ethylenediamine reacts with dimethyldichlorosilane in xylene to form a linear polymeric silylamine of the composition $(CH_3)_2SiNHCH_2CH_2NH$. Reaction of this with anhydrous $CuCl_2$ brings about rapid rearrangement to form a polymeric silazane and eliminate half of the ethylenediamine as Cu^{++} complex. Subsequent treatment of the silazane with excess $CuCl_2$ results in reversible coördination, with cross-linking. Copper-free silazane polymer hydrolyzes only $^1/_3$ as fast as the original silylamine, probably through decreased donor activity because of greater involvement of the nitrogen electron-pairs with silicon.

Numerous organosilicon compounds containing silicon–nitrogen bonds have been prepared, principally through the reaction of organochlorosilanes with ammonia or amines. In general, such compounds are thermally quite stable but hydrolyze at varying rates to form the corresponding siloxane and regenerate ammonia or the amine. Such behavior implies variable donor properties on the part of nitrogen linked to silicon in the different structures; for example, trisilylamine appears to have no donor tendency at all.[1] The purpose of the present series of investigations is to determine whether the nitrogen atoms in *polymeric* organosilazanes and organosilylamines retain any donor properties toward metal ions, and, if so, whether coördination to such metal ions affects the structure or the properties of such polymers.

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[1] S. Sujishi and S. Witz, THIS JOURNAL, **79**, 2447 (1957).