drides prepared by certain methods consist of hydrogen and arsine occluded in cracks and holes in arsenic particles, but it is difficult to explain the very hydrogen-rich solids of composition $AsH_{0.5}$ in this manner. When macro amounts of these latter hydrides are available, various physical-chemical studies may elucidate their structure.

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

The Reaction of Silylamines with Boron Trifluoride. Methyl- and Silylaminoboron Difluorides

BY SEI SUJISHI AND SAMUEL WITZ

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N-Silyldimethylamine, N-methyldisilylamine and trisilylamine react with boron trifluoride to yield dimethylaminoboron difluoride, N-methylsilylaminoboron difluoride and disilylaminoboron difluoride, respectively, and silyl fluoride. The variation in the physical properties of the aminoboron difluorides is discussed. Silylaminoboron difluorides decompose to form borazole derivatives and silyl fluoride. New vapor pressure data for silyl fluoride and N,N′,N″-trimethyl-B,B′,B″-trifluoroborazole were obtained.

With trimethylboron as the reference acid, the base strengths of silylamines show the following order: $(CH_3)_3N > (SiH_3)(CH_3)_2N > (CH_3)(SiH_3)_2N \sim (SiH_3)_3N$.[1] Neither methyldisilylamine nor trisilylamine forms an addition compound with trimethylboron and, therefore, their relative base strengths are not known.

With the object of completing this order, the reactions of the silylamines with boron trifluoride were investigated. Boron trifluoride appeared to be a suitable reference acid since Burg and Kuljian had reported that trisilylamine–boron trifluoride forms reversibly in the range −78 to −40° with a solid–gas equilibrium pressure of 3.7 mm. at −55°.[2] Although we found evidence for the formation of amine–boron trifluoride addition compounds, we could not measure the equilibrium pressures. This difficulty arose because secondary reactions, which yield aminoboron difluorides and silyl fluoride, occurred too rapidly. The nature of this secondary reaction is similar to that reported for the silylamine–boron trichloride system[2] and is the subject of the present paper.

Results and Discussion

Reaction of Silylamines with Boron Trifluoride.—Silyldimethylamine, methyldisilylamine and trisilylamine all absorbed an equimolar quantity of boron trifluoride at −80° to form white solids. Silyl fluoride was liberated slowly and at −80° less than an equivalent of it was formed in 16 hours.

When the amine–boron trifluoride mixtures were warmed to 25° about an equivalent of silyl fluoride was obtained. The formation of silyl fluoride was rapid in the methyldisilylamine and silyldimethylamine systems but was slow in the trisilylamine system. In the trisilylamine–boron trifluoride system, the total pressure indicated that trisilylamine–boron trifluoride was completely dissociated at partial pressures of 27 mm. of the components. After several days, however, almost an equivalent of silyl fluoride was obtained.

Along with silyl fluoride, substituted aminoboron difluorides were obtained. Dimethylaminoboron difluoride,[3] N-methylsilylaminoboron difluoride and disilylaminoboron difluoride were isolated from the silyldimethylamine, methyldisilylamine and trisilylamine systems, respectively. The silylaminoboron difluorides have not previously been reported in the literature.

The results suggest that the reactions of the silylamines with boron trifluoride proceed in two steps: (1) absorption of boron trifluoride to form an addition compound and (2) the elimination of silyl fluoride from the addition compound to form aminoboron difluoride.

$$(SiH_3)_3N: + BF_3 = (SiH_3)_3N:BF_3 \qquad (1)$$

$$(SiH_3)_3N:BF_3 = SiH_3F + (SiH_3)_2N{=}BF_2 \qquad (2)$$

The heats of formation of the addition compounds in the gas phase, from the amine and boron trifluoride, can be estimated and correlated with the results. According to Brown and Johannesen, the heat of formation of trimethylamine-boron trifluoride is −28 kcal./mole.[4] We have suggested that the substitution of a silyl group for a methyl group increases the heat of formation by about 9 kcal. for each successive substitution.[1] Hence, the approximate heat of formation of silyldimethylamine–boron trifluoride is −19 kcal., for methyldisilylamine–boron trifluoride −10 kcal., and for trisilylamine–boron trifluoride −1 kcal.

The last value is compatible with the observed gas phase non-association in the trisilylamine–boron trifluoride system.[5] The rapid formation of silyl fluoride in the methyldisilylamine–boron trifluoride and silyldimethylamine–boron trifluoride systems at 25° is compatible with heats of for-

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[1] S. Sujishi and W. Witz, THIS JOURNAL, **76**, 4631 (1954).

[2] A. B. Burg and E. S. Kuljian, *ibid.*, **72**, 3103 (1950).

[3] (a) J. F. Brown, Jr., *ibid.*, **74**, 1219 (1952); (b) A. B. Burg and J. Banus, *ibid.*, **76**, 3903 (1954).

[4] H. C. Brown and R. B. Johannesen, *ibid.*, **75**, 16 (1953).

[5] The value of −1 kcal. for the heat of formation of trisilylamine–boron trifluoride appears on first consideration to be too small to account for the formation of the solid adduct at −80°. However, A. B. Burg and Sr. A. A. Green (*ibid.*, **65**, 1838 (1943)) report that trimethylamine–boron trifluoride molecules form associated aggregates even in the gas phase. In the solid state, therefore, strong dipole forces between the addition compound molecules could stabilize the adduct.

mation of the addition compounds. Steps 1[6] and 2 both occur rapidly in these systems. The elimination of silyl fluoride may be comparably rapid from trisilylamine–boron trifluoride, but because of the low concentration of the addition compound the over-all rate is slow.

We conclude that, with boron trifluoride as the reference acid, methyldisilylamine is a stronger base than trisilylamine.

Aminoboron Difluorides.—The volatility of the substituted aminoboron difluorides increases in a striking manner with successive replacement of methyl groups by silyl groups. Thus, at 0° the vapor pressures are 0.2 mm. for solid dimethylaminoboron difluoride, 23 mm. for solid methylsilylaminoboron difluoride and 230 mm. for liquid disilylaminoboron difluoride. The high vapor pressure of disilylaminoboron difluoride is especially noteworthy. It is greater than that of either trisilylamine (110 mm.) or of methyldisilylamine (193 mm.) at 0°.[1]

The heats of vaporization and the melting points of dimethylaminoboron difluoride (19.1 kcal. and 160–164°) and disilylaminoboron difluoride (7.2 kcal. and $< -120°$) also show marked difference. Unfortunately corresponding values could not be determined for methylsilylaminoboron difluoride because of its instability toward decomposition. However, it was noted that methylsilylaminoboron difluoride was a solid at 25°.

The physical properties suggest that in the condensed state, dimethylaminoboron difluoride molecules are associated by strong intermolecular forces, while disilylaminoboron difluoride molecules are unassociated and held together by ordinary van der Waals forces. The interaction between methylsilylaminoboron difluoride molecules appears to be intermediate between these two extremes.

Previous workers have not agreed on the state of aggregation of dimethylaminoboron difluoride in the solid. Brown[3a] has assumed that dimethylaminoboron difluoride is dimeric while Burg and Banus[3b] have assumed that it is monomeric. Both of these conclusions were extrapolated from vapor density results. Brown's data were obtained at 155° and 747 mm. while Burg and Banus do not state the conditions of their experiments. Our data show that at low pressures (35 mm. at 96°), monomers are the chief species in the gas phase, while at moderate pressures (141 mm. at 136°) dimers occur to the extent of about 30%.

Convincing evidence for the association of dimethylaminoboron difluoride in the solid may be obtained by examination of the properties of aminoboron dichlorides. There is very little difference in the physical properties of monomeric dimethylaminoboron dichloride (m.p. −43°, v.p. 26 mm. at 25°)[7] and disilylaminoboron dichloride (m.p. $< -78°$, v.p. 22 mm. at 25°).[2] In contrast, dimeric dimethylaminoboron dichloride is much less volatile (v.p. 1 mm. at 90°)[7] and higher melting (m.p. 142°).[7] On the basis of these facts, it would be expected that the properties of monomeric dimethylaminoboron difluoride and disilylaminoboron difluoride should be similar. The enormous difference actually observed, therefore, indicates that dimethylaminoboron difluoride is associated in the solid state.

Wiberg and Schuster[8] and Brown and Osthoff[7] have suggested that the dimerization of dimethylaminoboron dichloride occurs through nitrogen–boron coördinate bond formation. We assume that the association of dimethylaminoboron difluoride also occurs through nitrogen–boron coordinate bonds. Without specifying the nature of the molecular unit in the solid, but assuming only that all possible coördinate bonds are formed, as for example in cyclic polymers or linear polymers, it is possible to estimate the heat of dissociation of such bonds between dimethylaminoboron difluoride molecules. The estimation is made in the same way as the value for the proposed nitrogen–silicon coördinate bond in silyldimethylamine was obtained.[1] For dimethylaminoboron difluoride, the heat of dissociation thus obtained is 10.5 kcal./mole of nitrogen–boron bond.

The estimated value of 10.5 kcal. for dimethylaminoboron difluoride can now be used to explain the variation in the physical properties of the silylaminoboron difluorides. In methylsilylaminoboron difluoride, the silyl group stabilizes the monomer by 9 kcal./mole and the nitrogen–boron coordinate bond energy decreases to 1.5 kcal. Similarly in disilylaminoboron difluoride, the two silyl groups reduce the heat of dissociation to −7.5 kcal. and, hence, disilylaminoboron difluoride shows no association.

Decomposition of Aminoboron Difluorides.—The silylaminoboron difluorides decomposed to form borazole derivatives and silyl fluoride. This reaction is similar to the decomposition of silylaminoboron dichlorides.[2] Thus, methylsilylaminoboron difluoride yielded N,N′,N″-trimethyl-B,B′,B″-trifluoroborazole, a compound previously reported by Wiberg and Horeld,[9] and disilylaminoboron difluoride yielded N,N′,N″-trisilyl-B,B′,B″-trifluoroborazole. The quantity of the last compound was too small to characterize the compound.

The rate of formation of silyl fluoride was rapid from methylsilylaminoboron difluoride and slow from disilylaminoboron difluoride. Burg and Kuljian[2] found that methylsilylaminoboron dichloride decomposed more rapidly than disilylaminoboron dichloride. These differences in rate may be rationalized by the mechanism suggested below.

Mechanism of Elimination of Silyl Fluoride.—When silylamines form addition compounds with boron trifluoride, the electron density on the fluorine atom should be relatively large and the electron density on the silicon atom relatively small. The fluorine atoms have three pairs of unshared electrons and, hence, may form coordinate bonds in the transition state with the silicon atom, using its 3d orbitals,[10] either in the same molecule or in a different molecule. The elimination of silyl fluoride is facilitated in this

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[6] The rate of formation of trimethylamine–boron trifluoride has been found to be very rapid with only a small activation energy; G. B. Kistiakowsky and R. Williams, *J. Chem. Phys.*, **23**, 334 (1955).

[7] C. A. Brown and R. C. Osthoff, THIS JOURNAL, **74**, 2340 (1952).

[8] E. Wiberg and K. Schuster, *Z. anorg. Chem.*, **213**, 77 (1933).

[9] E. Wiberg and G. Horeld, *Z. Naturforsch.*, **6B**, 338 (1951).

[10] C. G. Swain, R. M. Esteve, Jr., and R. H. Jones, THIS JOURNAL, **71**, 965 (1949).

TABLE I

CONDITIONS FOR SEPARATION OF COMPOUNDS

System	$(SiH_3)_3N-BF_3$		$(CH_3)(SiH_3)_2N-BF_3$		$(SiH_3)(CH_3)_2N-BF_3$
Compd.	$(SiH_3)_2NBF_2$	$(SiH_3NBF)_3$	$(CH_3)(SiH_3)NBF_2$[a]	$(CH_3NBF)_3$	$(CH_3)_2NBF_2$
Dist. T, °C.	− 80	25	25	25	25
Cond. T, °C.	−126	−80	−126	−80	−80

[a] Methylsilylaminoboron difluoride was purified by distillation through a trap at −80° and condensation in a trap at −126°.

way. As indicated earlier the rate-determining step in the over-all reaction, of silylamines with boron trifluoride, is the formation of the addition compound.

The decomposition of silylaminoboron difluorides may be interpreted similarly. Silyl fluoride is eliminated from the dimer. This is followed by the association of the resultant boron-nitrogen derivative with another mole of silylaminoboron difluoride and the elimination of silyl fluoride from the adduct. The rate-determining step is the formation of the dimer. Since silylmethylaminoboron difluoride dimerizes more readily than disilylaminoboron difluoride, the rate of elimination of silyl fluoride from the former is greater than from the latter.

Experimental Part

A Stock type high vacuum line was employed. The silylamines were prepared and purified by methods described previously.[1] Boron trifluoride (Matheson Co., Inc.) was purified in the vacuum line and a tensiometrically homogeneous sample (v.p. obsvd. 300 mm. at −111.8°, lit.[11] 300 mm.) obtained.

The various products of the reactions were separated and purified by fractional distillation and condensation. Silyl fluoride, which was obtained in all of the reactions, was isolated by distillation at either −126 or −117°. The pertinent data for the separation of the other compounds are summarized in Table I.

Silyl fluoride was purified by the method described in the section on the vapor pressure of silyl fluoride. When the presence of boron trifluoride was suspected, the silyl fluoride fraction was treated with a measured quantity of ethyl ether. The ethyl ether combined with the boron trifluoride to form ethyl ether–boron trifluoride. The silyl fluoride, ethyl ether and ethyl ether–boron trifluoride were separated by distillation and the quantity of boron trifluoride originally present was calculated from the results of the separation. This method will be referred to as the ethyl ether test for boron trifluoride.

All quantities expressed in cc. are those for the gas at S.T.P. These volumes are accurate to ±0.2 cc.

Silyldimethylamine–Boron Trifluoride System.—Silyldimethylamine, 10.6 cc., and 10.6 cc. of boron trifluoride were combined and kept at −80°. A white solid was observed and the pressure remained constant at 98 mm. (6 cc.) for 15 hours. The pressure did not change significantly as the temperature was raised. Thus, at −55° it was 97 mm. and at −30° it was 109 mm. The mixture was warmed to 22°. The pressure rose to 198 mm. (11.9 cc.) and a white crystalline solid was observed.

The mixture was fractionated and 11.0 cc. of crude silyl fluoride and an unmeasured quantity of dimethylaminoboron difluoride were obtained. The crude silyl fluoride was found to contain 0.3 cc. of boron trifluoride (ethyl ether test), 1.3 cc. of silane, 6.0 cc. of pure silyl fluoride (v.p. 29 mm. at −126°) and 3.4 cc. of a mixture of silyl fluoride and polyfluorosilane (v.p. 23 mm. at −126.3°).

Dimethylaminoboron Difluoride.—The dimethylaminoboron difluoride was identified by its v.p. (obsd. 4.2 mm. at 55° and 20.0 mm. at 70° lit.[3b] 3.8 and 19.1 mm., respectively) and its m.p. (obsd. 146–149°, 160–165°, 164–165°, lit. 155° (Burg)[3b] and 167–169° (Brown)[3a]). The heat of sublimation may be calculated to be about 19 kcal./mole of monomer gas.

In a similar expt., 24.4 cc. of boron trifluoride and 24.4 cc. of silyldimethylamine reacted at 25° in 5 minutes to yield 0.9 cc. of silane, 23.3 cc. of silyl fluoride, 0.3 cc. of polyfluorosilane, and dimethylaminoboron difluoride. The dimethylaminoboron difluoride was tensiometrically homogeneous with a v.p. of 8.3 mm. at 65.1°. The vol. of the gas was 20.8 cc. at 136° and 141 mm. and 21.3 cc. at 161° and 154 mm. Using the initial quantities of boron trifluoride and silyldimethylamine as the base, it may be calculated that the dimethylaminoboron difluoride was about 30% dimerized.

Methyldisilylamine–Boron Trifluoride System.—Methyldisilylamine, 17.8 cc., and 17.8 cc. of boron trifluoride were kept at −80°. The pressure slowly rose to 32 mm. in 2 hours and to 49 mm. (10 cc.) in 16 hours. A white solid was observed. The mixture was distilled at −126° and 10.1 cc. of distillate which contained 0.3 cc. of silane, 9.7 cc. of silyl fluoride and 0.1 cc. of polyfluorosilane was obtained. All of the fractions were recombined and the mixture warmed to 27°. After 10 min., the pressure became constant at 174 mm. (35.2 cc.). A very small quantity of white solid failed to vaporize. After 45 min. at 27°, the mixture was fractionated. Silane, 0.2 cc., silyl fluoride, 23.8 cc., polyfluorosilane, 0.5 cc., and crude methylsilylaminoboron difluoride, 10.9 cc., were obtained.

Methylsilylaminoboron Difluoride.—The crude methylsilylaminoboron difluoride was purified by distillation at −80°. In 15 minutes, 1.7 cc. of distillate was obtained and in the next 1/2 hour no further quantity of volatile fraction was obtained. The residue, 7.8 cc., was pure methylsilylaminoboron difluoride. It was a white solid at 0° and was tensiometrically homogeneous with a v.p. of 23.0 mm. The mol. wt. by vapor density measurement at 27° and 106 mm., was 108 (calcd. for $(CH_3)(SiH_3)NBF_2$ 109.0).

Methylsilylaminoboron difluoride decomposed slowly even at 0°. All of the material present in the crude methylsilylaminoboron difluoride fraction were combined and the mixture allowed to stand at 27°. After 20 hours, white crystals were observed and by fractionation, 4.1 cc. of silyl fluoride was isolated. After 5 days a total of 10.7 cc. of silyl fluoride. 0.2 cc. of methylsilylaminoboron difluoride and 3.2 cc. of crude N,N′,N″-trimethyl-B,B′,B″-trifluoroborazole were obtained.

N,N′,N″-Trimethyl-B,B′,B″-trifluoroborazole.—The crude trimethyltrifluoroborazole, 3.2 cc., was purified by distillation at −23°. A tensiometrically homogeneous sample (v.p. 0.25 mm. at 0°) was obtained. The v.p. were measured at various temperatures. The results may be expressed by the equation $\log P_{\text{mm}} = -3165.2/T_{°\text{K}} + 10.8256$. The results are summarized in Table II. The mol. wt., by vapor density measurement at 64° and 15.6 mm., was 176 (calcd. for $(CH_3NBF)_3$, 176.6). The heat of vaporization is calculated to be 14.5 kcal. The m.p. in an evacuated and sealed capillary tube was 88–89° (lit. 85°).[12]

TABLE II

VAPOR PRESSURE OF $(CH_3NBF)_3$

T, °C.	0.0	25.1	34.8	44.6	54.7
P_{mm}, obsd.	.25	1.6	3.6	7.3	14.9
P_{mm}, calcd.	.17	1.6	3.5	7.4	14.9

In a duplicate experiment, 12.5 cc. of methyldisilylamine and 12.5 cc. of boron trifluoride reacted to yield as the final products 22.8 cc. of silyl fluoride, 1.8 cc. of silylmethylaminoboron difluoride and 3.4 cc. of trimethyltrifluoroborazole.

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

[12] The physical constants reported for N,N′,N″-trimethyl-B,B,′-B″-trifluoroborazole (ref. 9) are m.p. 85°, v.p. 6 mm. at 69° and 320 mm. at 186°. Although the m.p. observed by us is in fair agreement with the value reported, the v.p. show very poor agreement.

Trisilylamine–Boron Trifluoride System.—Boron trifluoride, 14.4 cc., and trisilylamine, 14.4 cc., were combined and kept at −80°. After 0.6 hour the pressure reached a minimum value of 22 mm. and a white solid formed. The pressure slowly increased and in 1.6 hours was 26 mm. (5 cc.). The mixture was distilled at −126° and 5.9 cc. of silyl fluoride was obtained (v.p. at −123.2°, obsd. 42.5 mm., SiH_3F 43.1 mm.). The absence of boron trifluoride was confirmed by the ethyl ether test.

The residue was a solid at −80° and exerted a pressure of 1.9 mm. This was examined for homogeneity by distilling small quantities away at −80° and measuring the pressure over the solid after each distillation at −53.7°. The pressure varied from 12.8 to 2.2 mm. and, hence, the solid was not homogeneous. All of the fractions were combined and the total gas volume was measured. At 27° and 113.5 mm. the volume was 22.8 cc. (This value combined with the volume of silyl fluoride recovered initially, 5.9 cc., yields a total of 28.7 cc. The sum indicates that there was no net change in the number of moles of gas in the system. As it will be shown below, silyl fluoride is produced by reaction 2. Since all of the components of reaction 1 are volatile at 27°, the fact that only a portion of the silyl fluoride expected for complete reaction was obtained shows that trisilylamine and boron trifluoride must coexist as gases without association. The partial pressure of the components may be calculated to be 27 mm.)

The mixture, 22.8 cc., was kept at 27° and periodically analyzed for silyl fluoride. The additional quantity of silyl fluoride obtained was 4.5 cc. after one hour and 7.2 cc. after 5 days. (The total quantity of silyl fluoride obtained thus far was 13.1 cc. or 0.93 equivalent of the starting components.)

Heating the residue after the separation of silyl fluoride did not appreciably effect the rate of formation of silyl fluoride. Thus, 4 hours at 55° gave 0.8 cc., 24 hours at 75° gave 2.2 cc., 24 hours at 85° gave 0.1 cc. and 18 hours, at 115° gave 0.5 cc. of silyl fluoride, respectively.

A total of 16.7 cc. of silyl fluoride and 12.5 cc. of other products was obtained. The 12.5-cc. fraction was separated into 11.9 cc. of disilylaminoboron difluoride and 0.6 cc. of borazole derivative.

Disilylaminoboron Difluoride.—The 11.9-cc. fraction was identified as disilylaminoboron difluoride by vapor density measurement. The mol. wt. was 124 at 23° and 144 mm. (calcd. for $(SiH_3)_2NBF_2$, 125.0). The vapor pressures of the compound, a liquid down to −120°, were measured. The results can be represented by the equation log $P_{mm} = -1563/T_{°K} + 8.102$ and are given in Table III. The heat of vaporization is 7.2 kcal.

Table III

Vapor Pressure of $(SiH_3)_2NBF_2$ (Liquid)

T, °C.	−52.5	−49.3	−30.9	−23.4
P_{mm}, obsd.	11.1	13.2	45.8	69.9
P_{mm}, calcd.	10.5	13.2	44.8	70.0

Disilylaminoboron difluoride decomposed very slowly when it was stored as a gas at room temperature. One of the products of the decomposition was silyl fluoride. The other product was undoubtedly N,N′,N″-trisilyl-B,B′,B″-trifluoroborazole, although the quantity obtained was too small to permit positive identification. The decomposition reaction may be written as

$$3(SiH_3)_2NBF_2 = 3SiH_3F + (SiH_3NBF)_3 \qquad (3)$$

The quantities of products isolated may be accounted for by equations 2 and 3. Thus, assuming that reaction 2 proceeded to completion, the quantity of disilylaminoboron difluoride which decomposed according to equation 3 should be 14.4 − 11.9 = 2.5 cc. The total quantity of silyl fluoride recovered then should be 14.4 + 2.5 = 16.9 cc. (obsd., 16.7 cc.) and that of the borazole derivative 0.8 cc. (obsd., 0.5 cc. in the trap at −80°).

In a duplicate expt., 13.6 cc. of trisilylamine and 13.6 cc. of boron trifluoride reacted to yield 18.0 cc. of silyl fluoride, 9.8 cc. of disilylaminoboron difluoride and a small quantity of the borazole derivative (v.p. 2.5 mm. at 24°). The borazole derivative was hydrolyzed with aqueous ammonium hydroxide and 10.8 cc. of hydrogen was obtained. Using the quantity of disilylaminoboron difluoride isolated as the base, it may be calculated that 17.4 cc. of silyl fluoride (obsd., 18.0 cc.) and 1.27 cc. of the trisilyltrifluoroborazole should have been obtained. The last compound on hydrolysis should yield 11.4 cc. of hydrogen (obsd., 10.8 cc.).

Disilylaminoboron Difluoride–Boron Trifluoride System.—Disilylaminoboron difluoride did not react with boron trifluoride at moderate pressure at either 26 or −80°. Thus, when 9.8 cc. of disilylaminoboron difluoride and 9.8 cc. of boron trifluoride were combined at 26° the total pressure remained constant at 169 mm. (19.6 cc.) for 18 hours. By fractional condensation, 9.2 cc. of boron trifluoride was isolated from the mixture.

Similarly, when 9.8 cc. of disilylaminoboron difluoride and 9.5 cc. of boron trifluoride were kept at −80°, the total pressure of 48 mm. (9.8 cc.) indicated that the boron trifluoride was not soluble in liquid disilylaminoboron difluoride. After three days at −80°, 9.8 cc. of boron trifluoride was isolated from the mixture.

Disilylaminoboron difluoride and boron trifluoride did react, however, at −80° when the partial pressure of boron trifluoride was high. Disilylaminoboron difluoride, 9.8 cc., and 64.4 cc. of boron trifluoride were sealed in an ampoule of 6-cc. volume and kept at −80° for five days. (The v.p. of boron trifluoride is roughly 4.5 atm. at this temp.) After the first day white crystals and a colorless liquid phase were observed. On distillation at room temperature 73.2 cc. of gas was recovered from the ampoule. A small quantity of grayish white residue was left in the ampoule. Fractionation yielded 0.5 cc. of unidentified product (volatile at 25°, non-volatile at −80°), 3.4 cc. of disilylaminoboron difluoride (v.p. obsd. 15.5 mm. at −45.4°, calcd. 17 mm.), 57.4 cc. of boron trifluoride (ethyl ether test), 1.5 cc. of silane, 7.5 cc. of silyl fluoride (v.p. obsd., 28.9 mm. at −127.5°, calcd. 28 mm.), and 1.6 cc. of polyfluorosilane (v.p. obsd., 15 mm. at −127.2°).

The results of the experiment indicate that 7.0 cc. of boron trifluoride reacted with 6.4 cc. of disilylaminoboron difluoride to yield 7.5 cc. of silyl fluoride, and 3.1 cc. of silane and polyfluorosilane and other products.

Vapor Pressure of Silyl Fluoride.—The vapor pressures of silyl fluoride obtained in the present work differed considerably from those reported by Emeleus and Maddock.[13] Emeleus and Maddock obtained silyl fluoride from the reaction of silyl chloride with antimony trifluoride and state that the purity of the product did not exceed 98%.

The different fractions of silyl fluoride isolated from the experiments were combined and purified by distillation through a series of traps kept at −126, −160 and −196°. The major portion of the silyl fluoride condensed in the −160° trap along with some less volatile material. The silyl fluoride was recovered from this by slow distillation at −160°. A tensiometrically homogeneous sample was thus obtained. The purity was further established by mol. wt. determination and by hydrolysis. The mol. wt. at 24° and 80.6 mm. was 50.0 (calcd. for SiH_3F, 50.08). Hydrolysis with saturated aqueous sodium hydroxide at 30–40° for 45 min. of 8.84 cc. and 11.57 cc. samples gave 26.5 cc. (calcd., 26.5 cc.) and 34.4 cc. (calcd., 34.7 cc.) of hydrogen, respectively.

The vapor pressures of the liquid were measured and the results can be expressed by the equation log $P_{mm} = -984.86/T_{°K} + 8.2001$. The results are summarized in Table IV. The extpd. b.p. is −88.1° and the heat of vaporization is 4.5 kcal./mole. Emeleus and Maddock reported −98.6° and 4.5 kcal., respectively, for these two values.[13]

Table IV

Vapor Pressure of SiH_3F (Liquid)

T, °C.	−127.2	−119.8	−117.8	−112.3
P_{mm}, obsd.	28.5	60.3	72.2	120.0
P_{mm}, calcd.	28.5	60.3	72.2	120.0

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Chicago 16, Illinois

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(13) H. J. Emeleus and A. G. Maddock, *J. Chem. Soc.*, 293 (1944).