[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF SOUTHERN CALIFORNIA]

The Reaction of Boron Trifluoride with Tetramethylaminoborine

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Tetramethylaminoborine (m.p. −92.2°; b.p. 65.0°) reacts with BF_3 at low temperatures to form the solid adduct $(CH_3)_2NB(CH_3)_2 \cdot BF_3$ which is stable at −78.5°. At higher temperatures this adduct loses BF_3 *in vacuo* or decomposes irreversibly to form $(CH_3)_2BF$ and $(CH_3)_2NBF_2$ (m.p. 165–168°; subl. p. est. 132°; monomer, contrary to the literature). This fluoride-shift reaction is clean and quantitative in the presence of BF_3, which suppresses the reversible dissociation and prevents the formation of oily and crystalline by-products. Pure $(CH_3)_2NBF_2$ is stable at 25°, but in ether solution it slowly decomposes to form a number of products, apparently including $BN \cdot (CH_3NBF)_x$ and $(CH_3)_3NBF_3$. When heated with $(CH_3)_3N$, it disproportionates to form $(CH_3)_3NBF_3$ and the new compound $[(CH_3)_2N]_2BF$ (m.p. −44.3°; b.p. 106°), the decomposition of which occurs readily in at least two ways, but is sharply limited by the reverse processes. With excess BF_3, it is cleanly converted back to $(CH_3)_2NBF_2$. These results suggest new interpretations of some of the products of the reaction of BF_3 with $(CH_3)_2NBH_2$.

Boron trifluoride has been found to react with certain compounds of electron-donor elements, with movement of fluoride from one atom to another. Examples are its reactions with $(CH_3BO)_3$ to form CH_3BF_2,[1] or with $(CH_3)_2BOB(CH_3)_2$ to form $(CH_3)_2BF$,[1] with $[(CH_3)_2N]_3SiH$ to form $HSiF_3$,[2] and with $(SiH_3)_3N$ to form other fluorosilanes.[3] Similar fluoride-shift reactions are known also for certain organic compounds containing the CO group.[4] Boron trifluoride adducts are assumed to be intermediates in all such reactions, but in most cases these adducts either could not be recognized or were not sought.

The present paper describes the formation and manner of decomposition of the BF_3-adduct $(CH_3)_2NB(CH_3)_2 \cdot BF_3$, along with certain of its chemical consequences. At low temperatures (*e.g.*, −46°) it dissociates *in vacuo* into its original components; but at higher temperatures (*e.g.*, 0°) in a closed system it undergoes a fluoride-shift reaction yielding almost exclusively $(CH_3)_2BF$ and $(CH_3)_2NBF_2$. The latter occurs only as a monomer, contrary to the literature and the analogy to the dimeric $(CH_3)_2NBCl_2$.[5] It decomposes fairly easily (but to a limited extent) under mild heating in the presence of impurities associated with its formation, but it seems to be stable at room temperature if highly purified. In an atmosphere of boron trifluoride it can be heated to its melting point (near 168°) without serious decomposition.

The stabilizing effect of boron trifluoride upon dimethylaminoboron difluoride may be explained at least partially in terms of a suppression of the disproportionation reaction $2(CH_3)_2NBF_2 \rightleftarrows [(CH_3)_2N]_2BF + BF_3$. Although this reaction is scarcely observable under ordinary circumstances, it can be pushed forward almost to completion by the use of trimethylamine to remove the boron trifluoride, so that a good yield of the bis-dimethylaminoboron fluoride is obtained. This new compound proved to be unstable enough to account for a considerable decomposition of its antecedent, $(CH_3)_2NBF_2$, to which it could be almost quantitatively reconverted by reaction with boron trifluoride.

It is noteworthy that these aminoboron fluorides are at least as labile as the corresponding aminoboron hydrides,[6] and that they show a wider variety of decomposition products at moderate temperatures. The simple exchange of fluoride for amino groups on boron would be analogous to the disproportionations of the aminoboron hydrides, but we find here still another type of radical-shifting, in which methyl groups move from one nitrogen atom to another, just as fluoride moves from one boron atom to another. Thus $(CH_3)_2NBF_2$, extensively heated in an isolated system or left for a few days in ether solution at room temperature, forms $(CH_3)_3NBF_3$, $(CH_3NBF)_x$, apparently BN, and possibly other products. Also unusual is the behavior of $[(CH_3)_2N]_2BF$, the limited decomposition of which involves not only the exchange of fluoride for amino groups, but also a shift of methyl groups to form trimethylamine and $(CH_3NBF)_x$.

The new knowledge of the aminoboron fluorides permits a more realistic formulation of certain empirically-designated products of the previously-reported reaction of $(CH_3)_2NBH_2$ with BF_3.[6] The component previously written as $(R_2N)_2BF \cdot BF_3$ on the basis of its reaction with $(CH_3)_3N$ to yield a fraction apparently containing $(R_2N)_2BF$, now is recognized as $(CH_3)_2NBF_2$. Similarly, the fraction written as $(R_2N)_2BH \cdot BF_3$ probably should be $(CH_3)_2NBF_2 + (CH_3)_2NBHF$, especially in view of a recent unsuccessful attempt to regain $[(CH_3)_2N]_2BH$ from the supposed $[(CH_3)_2N]_2BH \cdot BF_3$. Further, the material previously designated as $(R_2N)_3B \cdot BF_3$ might better be regarded as a mixture of $[(CH_3)_2N]_2BF$ and $(CH_3)_2NBF_2$. Thus new light is thrown upon the complicated stoichiometry of the BF_3–$(CH_3)_2NBH_2$ reaction, which now seems more involved than ever, in view of the tendencies of the products to decompose in more than one manner.

Experimental Part

Preparation and Characterization of Tetramethylaminoborine.—The compound $(CH_3)_2NB(CH_3)_2$ has been prepared in this Laboratory by the reaction of dimethylamine with $(CH_3)_2BBr$,[7] with $(CH_3)_4B_2H_2$, and with $(CH_3)_3B$.[8]

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[1] A. B. Burg, THIS JOURNAL, **62**, 2232 (1940).

[2] A. B. Burg, "Fluorine Chemistry," J. H. Simons, editor, Academic Press, Inc., New York, N. Y., 1950, p. 109.

[3] A. B. Burg and E. S. Kuljian, THIS JOURNAL, **72**, 3104 (1950).

[4] (a) G. T. Morgan and R. B. Tunstall, *J. Chem. Soc.*, **125**, 1963 (1924); (b) G. T. Morgan and R. Taylor, *ibid.*, **141**, 1497 (1932); (c) J. R. Killelea, THIS JOURNAL, **70**, 1971 (1948); (b) H. Meerwein and D. Vossen, *J. prakt. Chem.*, **141**, 149 (1934).

[5] J. F. Brown, THIS JOURNAL, **74**, 1219 (1952).

[6] A. B. Burg and C. L. Randolph, Jr., *ibid.*, **73**, 953 (1951).

[7] T. E. Steinberg, M.S. Thesis, University of Southern California Libraries, 1947. The same thesis includes the first indication of the fluoride-shift reaction of tetramethylaminoborine with boron trifluoride.

[8] E. Wiberg and P. Buchheit, quoted by J. Goubeau, *FIAT Rev. Ger. Sci., Inorg. Chem., Part I*, 228 (1939–1946 (Pub. 1948)).

The third method (14 hours, 300°, 3 atm.) is most direct, but the first two are convenient if one happens to have $(CH_3)_2BBr$ or $(CH_3)_4B_2H_2$ on hand for other reasons. The second method gave an 89% yield when carried out in a bomb tube above atmospheric pressure (at 100°), but at a half-atmosphere the dissociation of the complex $(CH_3)_2NH \cdot HB(CH_3)_2$ permitted extensive disproportionation of the $HB(CH_3)_2$ unit[9] and the yield of the desired product fell to 56%.

The product from each of these methods contained a trace of more volatile impurity which correlated with the formation of solid material on standing. After repeated high-vacuum distillation in a small column having a reflux temperature of −78°, an analysis by hydrolysis to $(CH_3)_2BOH$ and $(CH_3)_2NH$ showed the product to be at least 99% pure.

Pure $(CH_3)_2NB(CH_3)_2$ melted sharply at −92.2°. Its observed molecular weight was 85.0 (gas density method, calcd. 84.96). The liquid showed no tendency to polymerize, during months in a sealed tube at room temperature. Air attacked it rapidly, without igniting it. Its vapor tensions, observed in the range −50 to 60°, determined the equation $\log p_{mm} = -(1905.3/T) + 1.75 \log T - 0.005271 T + 5.8722$, implying that the boiling point is 65.0° and the Trouton constant approximately 19.8 cal./deg. mole. A representative set of vapor tension values is given by Table I.

TABLE I

VAPOR TENSIONS OF $(CH_3)_2NB(CH_3)_2$

t, °C.	−50.4	−41.0	−21.2	0.0	14.9	39.75	58.5
$p_{mm.}$ (obsd.)	1.80	3.80	15.24	52.6	109.4	316.7	617.5
$p_{mm.}$ (calcd.)	1.79	3.82	15.30	52.6	110.6	316.7	617.3

The Formation of $(CH_3)_2NB(CH_3)_2 \cdot BF_3$.—The addition of BF_3 to $(CH_3)_2NB(CH_3)_2$ occurred smoothly as the mixture was warmed slowly from −196 to −78.5°. The absorption of BF_3 gas was signalled by a decrease of pressure at −120°. With equimolar proportions of the reactants, there was some residual gas, most of which was absorbed as the reaction tube was alternately cooled and warmed between −196 and −78°. With excess BF_3 the formation of the 1:1 adduct could be completed by warming to −60°, without risk of premature occurrence of the fluoride-shift reaction. Even at −46° this reaction was very slow, but the pure adduct began to develop a dissociation pressure (initial rate, 0.3% per minute) and a little BF_3 was distilled off and identified. With the removal of some BF_3, the remaining sample showed lower limiting pressures, ascribed to the slightly excessive proportion of $(CH_3)_2NB(CH_3)_2$ in the condensed phase.

Fluoride-shift Decomposition of the BF_3-Adduct.—In one experiment 28.5 cc.[10] each of BF_3 and $(CH_3)_2NB(CH_3)_2$ combined as described above, leaving 0.54 cc. of gaseous residue. The solid adduct was quickly warmed to 0° and at the end of two hours the gas was removed and identified as $(CH_3)_2BF$ (molecular weight 60.1; calcd. 59.88—vapor tensions 92.1 mm. at −78.5° and 21.6 mm. at −98.1°; known values, 93.0 and 21.4).[1] The yield of this totaled 28.2 cc., or 99%. In other experiments the gaseous product sometimes was contaminated with its disproportionation products, but it was always possible to show that the gaseous product of the first five to ten minutes of reaction was pure $(CH_3)_2BF$.

In all experiments involving the pure adduct, the main solid product was $(CH_3)_2NBF_2$, but it contained a trace of slightly volatile liquid and a solid melting at 45°. The latter increased upon heating for some days near 100°, reaching a limit roughly estimated as 30% of the whole. As shown later, this material represented the CH_3NBF stage of degradation. It proved to be barely volatile at 100°, so that $(CH_3)_2NBF_2$ could be separated from it by sublimation under high vacuum at room temperature.

The fluoride-shift reaction yielded pure $(CH_3)_2NBF_2$ only in the presence of excess BF_3. Thus a 65.1-cc. sample of the BF_3-adduct with 11.2 cc. of extra BF_3 was allowed to stand for 13 hours at −23° and then warmed to room temperature to finish the reaction. Although the gaseous product was an unresolvable mixture (presumably $MeBF_2$, Me_2BF, and BF_3), the solid product was 99% sublimable under high vacuum at room temperature and had the physical properties of pure $(CH_3)_2NBF_2$. Again, 75.7 cc. of $(CH_3)_2NB(CH_3)_2$ and 81.8 cc. of BF_3 were allowed to warm from −140 to −65° during four hours (leaving 6.9 cc. of unabsorbed gas) and then held successively at 0° for six minutes and at 25° for 20 minutes. Once more, the solid product was pure $(CH_3)_2NBF_2$. From the gas at the end of the six-minute period it was possible to isolate 45.0 cc. of nearly pure $(CH_3)_2BF$ (vapor tension 94 mm. at −78.5°), but the final gaseous product again was unresolvable. It would appear that the disproportionation of $(CH_3)_2BF$ was favored by some component of the system, since this gas usually can be kept for weeks at room temperature without change.

Analysis and Molecular Weight of $(CH_3)_2NBF_2$.—A sample of the barely-volatile white solid product of the fluoride-shift reaction was purified by sublimation under high vacuum, at temperatures not exceeding 40°, and hydrolyzed in the presence of KCl and $CaCl_2$ at 100° (14 hours); then nitrogen was determined by the Kjeldahl method, boron by titration of the mannitol spirane, and fluoride gravimetrically as CaF_2. Results: 0.812 mmole of N, 0.833 mmole of B, and 1.620 mmoles of F, all in the same unweighed sample.

For the molecular weight of $(CH_3)_2NBF_2$, the solid product of a known amount of $(CH_3)_2NB(CH_3)_2 \cdot BF_3$ was vaporized in the immersible tensimeter,[11] for measurement of the standard volume of the vapor. In one experiment the standard volume corresponded exactly to the theoretical molecular weight (92.8) and in others the results were close to this. Serious deviations occurred only when less volatile impurities could be recognized. The measurements were done quickly in order to minimize the formation of such contaminants.

Characterization of $(CH_3)_2NBF_2$.—The melting point of pure $(CH_3)_2NBF_2$ is rendered very uncertain by its instability. Often one can detect a trace of oily liquid at 145°, before the main melting occurs at 155°; thereafter one recognizes major proportions of the typical decomposition products. Under one atmosphere pressure of BF_3, however, a pure sample first shows a trace of liquid at 155° and melts chiefly in the range 165–168°—repeatable after a process of recrystallization within the same sealed container at 75°. The true melting point doubtless is still higher, but at least the present results serve as evidence that the product is the same as the material reported in the literature as $[(CH_3)_2NBF_2]_2$.[5]

The polarizing microscope disclosed the crystals of pure $(CH_3)_2NBF_2$ as mostly rhombuses whose angle was 82° 40′; the extinction direction bisected the crystal angles. They proved to be biaxial, and elongation in the vibration direction of the smaller refractive index sometimes was seen. When the heated vapor was cooled slowly, larger crystals developed, organizing as criss-cross fronds in which the individual rhombuses were easily seen.

The vapor tensions of $(CH_3)_2NBF_2$ were observed on several different samples, with results varying as much as 10% before and after heating as high as 120°. However, a fairly dependable set of values resulted from quick work with freshly resublimed samples, all at temperatures below 90°. Typical results, given in Table II, determine the equation $\log p_{mm} = 12.754 - 3995/T$, on which the calculated values are based. This implies a normal sublimation temperature of 132°, some 35° below the melting point.

TABLE II

VAPOR TENSIONS OF SOLID $(CH_3)_2NBF_2$

t, °C.	35.0	40.0	42.5	46.9	60.0	62.7	76.0	86.8
p_{mm} (obsd.)	0.63	1.03	1.23	1.87	5.76	7.20	20.4	46.0
p_{mm} (calcd.)	0.62	0.99	1.25	1.87	5.80	7.23	20.5	45.3

Behavior of $(CH_3)_2NBF_2$ in Ether.—Attempts to determine the molecular weight of $(CH_3)_2NBF_2$ in solution in ether, both by the isopiestic method (with azobenzene as the reference solute) and by direct measurement of the vapor tension lowering,[12] first indicated a monomer, but after a few days at room temperature the diminished vapor tension

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(9) A similar effect with $(CH_3)_2N \cdot HB(CH_3)_2$ was demonstrated by H. I. Schlesinger, N. W. Flodin and A. B. Burg, THIS JOURNAL, **61**, 1078 (1939).

(10) Throughout this paper the designation cc. refers to gases at standard conditions.

(11) A. B. Burg and H. I. Schlesinger, THIS JOURNAL, **59**, 785 (1937).

(12) Apparatus described by A. B. Burg, *ibid.*, **65**, 1630 (1943).

lowering indicated a polymer number as high as 2.34. By this time, however, a precipitate appeared, and could not be redissolved. After evaporation of the solution, only a small fraction of the original $(CH_3)_2NBF_2$ was found, but at least three other substances were present. One had the crystal habit and volatility of $(CH_3)_3NBF_3$. Another was far less volatile than this, but melted at 45° and by its crystal habit (fine matted mesh) could be recognized as one of the by-products of the formation of $(CH_3)_2NBF_2$. Finally, there was a non-volatile white solid which was strictly unaffected by heating *in vacuo* to the melting range of Pyrex. Since the ether was quantitatively recovered in pure condition, the refractory material could not have been an oxide. nor anything else except boron nitride. The indications thus strongly favored a disproportionation reaction in which the components of methyl fluoride were shifted from one molecule to another. Ether seems to be a catalyst for this reaction.

Analysis of $(CH_3NBF)_x$.—A 35.9-mg. sample of the material melting at 45° was isolated from the product of extensive heating of $(CH_3)_2NBF_2$, by sublimation *in vacuo*. It was hydrolyzed in a 30-ml. solution containing 0.934 meq. of HCl and 18 mmoles of $CaCl_2$ under reflux at 100° for 7 hours. The acid now was titrated to the methyl red end-point by 0.932 meq. of base, demonstrating no net yield of strong acid. Hence the acid liberated by hydrolysis of the B–F bond must have been equivalent to the amine liberated at the same time. The precipitated CaF_2 was collected and weighed as 25.0 mg., or 0.640 mmole of F. The amine was now boiled off from the alkaline solution and boron was determined by titration from the methyl red to the phenolphthalein end-point in the presence of mannitol, showing 0.660 mmole of B. These results correspond within reasonable error to the equation $2CH_3NBF + 6HOH + Ca^{++} \rightarrow CaF_2 + 2B(OH)_3 + 2CH_3NH_3^+$. Hence it appears that the substance was a polymer of the CH_3NBF unit; however in none of the present work has there been any appearance of the $(CH_3NBF)_3$ described by Wiberg and Horeld.[13]

Conversion of $(CH_3)_2NBF_2$ to $[(CH_3)_2N]_2BF$.—The reaction $2(CH_3)_2NBF_2 + (CH_3)_3N \rightarrow (CH_3)_3NBF_3 + [(CH_3)_2N]_2BF$ was not immediately observable at room temperature, but when 14.3-cc. samples of the reactants were heated in an immersible tensimeter,[11] small crystal-needles were seen at 100° and the decrease of pressure was complete after five hours at 130°. In conformity to the equation, 6.9 cc. of the amine was recovered, and the $(CH_3)_3NBF_3$ was recognized by its melting point (145–147°) and vapor tensions (5 mm. at 100° or 37 mm. at 140°).[14] The new compound $[(CH_3)_2N]_2BF$ was isolated by slow passage through a trap at −63° and condensation at −78.5°. Larger samples were obtained by flaming a tube containing $(CH_3)_2NBF_2$ with $(CH_3)_3N$ in slight excess, using the melting of the resulting $(CH_3)_3NBF_3$ as a warning against overheating. Under these conditions small yields of $[(CH_3)_2N]_3B$ also were obtained, and identified by comparison with the known vapor tensions and melting point of this compound.[15]

The composition of the new compound was evident from the stoichiometry of its formation, and was further confirmed by its nearly quantitative reconversion to $(CH_3)_2NBF_2$, as described in a later section. A 14.7-cc. sample weighed 78.2 mg.; mol. wt. 119.2 (calcd., 118.0).

Characterization of $[(CH_3)_2N]_2BF$.—The melting point of a freshly purified sample of bis-dimethylaminoboron fluoride was visually observed as −44.3 ± 0.1°. The slight but fairly rapid decomposition of this substance made it difficult to obtain good vapor tensions above 50°, but fairly good values were obtained at lower temperatures by exposing the sample to each elevated temperature only long enough for equilibration and measurement. The results, given by Table III, determine the equation $\log p_{mm} = 8.190 - 2013/T$, indicating the normal boiling point to be 106° and the Trouton constant 24.3 cal./deg. mole.

TABLE III

VAPOR TENSIONS OF $[(CH_3)_2N]_2BF$

t, °C.	12.3	17.8	25.0	36.2	43.3	37.1	51.7
p_{mm} (obsd.)	13.76	18.64	27.5	48.4	67.5	79.9	95.1
p_{mm} (calcd.)	13.74	18.71	27.6	48.3	67.5	80.2	98.4

The Instability of $[(CH_3)_2N]_2BF$.—On standing for an hour or two at room temperature, the liquid developed a trace of less volatile solid and a corresponding amount of gas which passed a trap *in vacuo* at −78.5°. Either at room temperature or at 100°, the decomposition seemed to stop when the gas amounted to 2% or less of the original sample volume. The gas had the odor and approximately the volatility of trimethylamine, but could not be ascribed to failure to remove a small excess of this reagent after formation of the bis-amino compound, since it formed again and again during ten repetitions of the incipient decomposition. The parallel product should have been a polymer of CH_3NBF; and in fact the least volatile product, after hydrolysis in the presence of $CaCl_2$, showed equivalent proportions (0.06 meq.) of B, F and amine. There were also indications of $(CH_3)_2NBF_2$ and $[(CH_3)_2N]_3B$. A full study of the decomposition of $[(CH_3)_2N]_2BF$ is in order, but is beyond the scope of the present paper.

Reconversion of $[(CH_3)_2N]_2BF$ to $(CH_3)_2NBF_2$.—A sample of $[(CH_3)_2N]_2BF$, estimated as 12.9 cc., was treated with 24.9 cc. of BF_3 in the immersible tensimeter[11] at −78.5°, with absorption of some 10 cc. of the BF_3 during five hours. Now the container was warmed to room temperature to complete the reaction. The unused BF_3 was removed at −78.5° and measured as 11.0 cc., meaning that 13.9 cc. reacted (8% beyond calcd.). The solid product was identified as pure $(CH_3)_2NBF_2$ by its vapor tensions (12.3 mm. at 69.6° and 33.7 mm. at 83.1°; calcd., 12.6 and 34.7) and melting-range ending at 168° in the presence of BF_3. The sample volume, measured at 120° and 220 mm. (saturated vapor would be 388 mm.) was 23.6 cc., or a 92% yield. Hence the equation $[(CH_3)_2N]_2BF + BF_3 \rightarrow 2(CH_3)_2NBF_2$ described the reaction, and at the same time the formula of the bis-aminoboron fluoride was confirmed.

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

[14] A. B. Burg and Sr. A. A. Green, THIS JOURNAL, **65**, 1838 (1943).

[15] A. B. Burg and C. L. Randolph, Jr., *ibid.*, **73**, 956 (1951).