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

Addition Compounds of Trimethylamine with Boron Fluoride and its Methyl Derivatives

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For the better understanding of chemical bonding, it is useful to make comparative studies of the complex-bonding powers of similar materials. The discovery of the methylboron fluorides, CH_3BF_2 and $(CH_3)_2BF$,[2] has made it possible to study the effect of substitution of methyl for fluoride upon the strength of the N→B bond in the series $(CH_3)_3NBF_3$, $(CH_3)_3NBF_2CH_3$, $(CH_3)_3NBF(CH_3)_2$, $(CH_3)_3NB(CH_3)_3$. The first of these compounds, $(CH_3)_3NBF_3$, was studied by Bright and Fernelius,[3] whose results show that the compound is strongly associated in solution. This conclusion is extended by our studies of the vapor-phase association of the same compound.

The vapor of $(CH_3)_3NBF_3$ is not measurably dissociated at temperatures as high as 230° (and probably higher). The vapor-phase dissociation of $(CH_3)_3NBF_2CH_3$ and $(CH_3)_3NBF(CH_3)_2$ was studied quantitatively; the relation of the results to the earlier data on $(CH_3)_3NB(CH_3)_3$[4] is discussed later in this paper. The dissociation pressures are not rigorously interpretable in terms of free energy values, because equilibria of the type $n(CH_3)_3NBX_3 \rightleftarrows [(CH_3)_3NBX_3]_n$, in which n is variable, influence the meaning of the results to an unknown, but probably small, degree. It is reasonable to assume that the substances here studied do not differ so much in this respect as to prevent fair comparisons of their stability.

Experimental Part

Apparatus.—All of the studies here reported were carried out by means of a high-vacuum manifold, consisting of a central pump-tube with stopcocks leading to several U-tubes placed in series, a long manometer with a very small adjacent condensation tube, joints for temporary attachment of bulbs and weighing tubes, an immersible manometric bulb,[5] and a vacuum tube-opener.[6] All stopcocks were lubricated by Apiezon L grease, which was not appreciably attacked. The volumes of separate parts of the U-tube system were determined by observing the pressures (not higher than 200 mm.) of weighed samples of pure sulfur dioxide. The manometric bulb was calibrated in the same manner.

Preparation of Materials.—Boron trifluoride was prepared from ammonium fluoborate, as described by Booth and Willson.[7] The product was condensed by liquid air, distilled into the vacuum system, and stored in a large bulb. Its vapor tension at −111.9° (m. p. of CS_2) was 303 mm., in agreement with the measurements by Pohland and Haarlos.[8]

Methylboron difluoride was prepared by the reaction of boron fluoride with methylboric anhydride (present in slight excess).[2] Pure dimethylboron fluoride was obtained by repeated fractionation of a three-year old sample remaining from the original preparation.[2] The purity of each sample was checked by measurement of the vapor tension at −78.5°.

Trimethylamine, obtained from a commercial 30% solution, was distilled free of water and stored in a sealed tube containing resublimed phosphoric anhydride (to remove N-H impurities).[9] It was introduced into the vacuum apparatus by means of the tube-opener. Its vapor tension at 0° was 680 mm. (cor.), in agreement with the results of Simon and Huter.[10]

Trimethylamine Boron Fluoride.—Precisely equal volumes of trimethylamine and boron fluoride (each 21.8 cc., or 0.97 millimole) were quantitatively condensed in the manometric bulb[5] (cooled by liquid air), and allowed to react during slow warming to room temperature. A white solid product was formed, without residual pressure. The bulb was wholly immersed in an oil-bath and the pressures were measured at various temperatures by means of a cathetometer. All values were corrected for the expansion and vapor pressure of mercury (applicability of the latter correction was assured by taking each reading only after heating for some time at higher temperatures). The vapor tensions of the solid $(CH_3)_3NBF_3$, given in Table I, determine the equation $\log_{10} p_{\text{mm.}} = 10.240 - \frac{3600}{T}$ from which the check values were calculated.

TABLE I

VAPOR TENSIONS OF SOLID $(CH_3)_3NBF_3$

t, °C.	100	109	130	134	140
p, mm. (obs.)	4.3	6.7	19.5	24.3	33.0
p, mm. (calcd.)	3.9	6.6	20.3	24.8	33.4

The vapor tensions of liquid $(CH_3)_3NBF_3$, given in Table II, determine the equation $\log_{10} p_{\text{mm.}} = 8.735 - (2963/T)$, from which the normal boiling point is estimated to be 233° and the Trouton constant, 25.5 cal./deg. mole.

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(1) This paper represents a thesis presented by Sister Agnes Ann Green (I.H.M.) to the Graduate Faculty of the University of Southern California, in partial fulfillment of the requirements for the degree of Master of Science, September, 1942.

(2) Burg, THIS JOURNAL, **62**, 2231 (1940).

(3) Bright and Fernelius, *ibid.*, **65**, 735 (1943).

(4) Schlesinger, Flodin and Burg, *ibid.*, **61**, 1079 (1939).

(5) Burg and Schlesinger, *ibid.*, **59**, 785 (1937).

(6) Stock, *Ber.*, **51**, 985 (1918).

(7) Booth and Willson, THIS JOURNAL, **57**, 2274 (1935).

(8) Pohland and Haarlos, *Z. anorg. allgem. Chem.*, **207**, 244 (1935).

(9) Ingram, Master of Science Dissertation, The University of Chicago Libraries, 1939.

(10) Simon and Huter, *Z. Elektrochem.*, **41**, 32 (1935).

Combination of this equation with that for the solid gives the heat of fusion as 3.5 kcal./mole, and the melting point as 150°. New samples, prepared from pure materials and resublimed, melted over the range 139–147° (sealed *in vacuo*). This broad but consistent range probably is due to the presence of associated forms of the substance, rather than to impurities. The high value of the Trouton constant indicates that the liquid may be more associated than the vapor, which, as next will be shown, is itself highly associated.

TABLE II

VAPOR TENSIONS OF LIQUID $(CH_3)_3NBF_3$

t, °C.	145	150	155	160	160[a]	165
p, mm. (obs.)	43.3	53.4	65.7	77.6	78.8	92.5
p, mm. (calcd.)	44.3	53.6	65.0	78.1	78.1	93.5

[a] Check measurement on a new sample.

The association of the vapor of $(CH_3)_3NBF_3$ is indicated by the data of Table III. As before, each pressure measurement was taken after cooling from a higher temperature, and corrected for the expansion and vapor pressure of mercury. The original sample (0.97 millimole of each component) was used here, and its weight, 0.1235 g., was determined afterward.

The molecular weight thus rather smoothly approaches the calculated value as the temperature rises, and there is no indication of any dissociation into the original amine and BF_3, such as might be observed at temperatures beyond the range of the apparatus here used. The 50% abnormality of the molecular weight, at a temperature just above the condensation point, together with the high value of the Trouton constant, would lead one to expect the liquid-phase molecular weight to average as high as twice that demanded by the formula $(CH_3)_3NBF_3$. The present results thus tend to confirm and supplement those of Bright and Fernelius.[3]

Trimethylamine Methylboron Difluoride.—Equal volumes (each 11.4 cc., or 0.51 millimole) of methylboron difluoride and trimethylamine were condensed together in a small reaction tube and allowed to warm slowly to room temperature. The result was a crystalline white solid which melted in the neighborhood of 35°. The residual pressure was negligible, but the product was sufficiently volatile to be distilled (at room temperature) into the manometric bulb, where the liquid–vapor equilibrium pressures (Table IV) were measured as in the preceding case. A second sample composed of 12.10 cc. (0.540 millimole) of each component, was prepared directly in the manometric bulb and employed for check measurements of the vapor pressures and for a study of the dissociation of the vapor. The results determine the equation $\log_{10} p_{\text{mm.}} = 8.523 - (2653/T)$, from which the "calcd." values of Table IV were derived. In view of the considerable degree of vapor-phase dissociation, the thermodynamic meaning of this equation is not perfectly clear, but it is presented for its descriptive value.

The vapor-phase dissociation of the compound $(CH_3)_3NBF_2CH_3$ was studied, using the 0.540 millimole sample which had been synthesized directly in the manometric bulb. The pressures were measured by the cathetometer, with the same precautions as those observed for $(CH_3)_3NBF_3$. From the known size of the sample, the volume of the bulb, and the pressure, the partial pressures of the three components were computed, on the assumption that the only process was $(CH_3)_3NBF_2CH_3 \rightleftarrows (CH_3)_3N + BF_2CH_3$. The equilibrium constants then were calculated according to the definition $K_{\text{atm.}} = \dfrac{P_{\text{amine}} \times P_{CH_3BF_2}}{P_{\text{complex}} \times 760}$. The five highest values of K determine the equation $\log_{10} K_{\text{atm.}} = 10.315 - (5045/T)$. The results and calculations are summarized in Table V.

Since the first two points in this series represented nearly saturated vapor, their deviation from the equation is not surprising, especially in view of the expectation that the process $n(CH_3)_3NBF_2CH_3 \rightleftarrows [(CH_3)_3NBF_2CH_3]_n$ would most affect these points. However, this association effect

TABLE III

APPARENT MOLECULAR WEIGHT OF $(CH_3)_3NBF_3$

t, °C.	170	175	180	190	200	220	230
p, mm. (cor.)	104.7	108.0	130.5	145.4	158.3	166.1	177.1
Vol. of container, cc.	170.6	171.1	170.7	170.7	171.0	171.1	171.0
Apparent mol. wt.	191.0	186.7	156.6	143.3	138.5	133.6	127.9
Mol. wt. obs./calcd.	1.50	1.47	1.23	1.13	1.09	1.05	1.01

TABLE IV

LIQUID–VAPOR EQUILIBRIUM PRESSURES OF $(CH_3)_3NBF_2CH_3$

t, °C.	34.0	39.5	41.0[a]	51.0	61.0	61.5[a]	70.0	72.3[a]	82.5	92.0	99.0
p, mm. (obsd.)	0.75	1.10	1.20	2.15	3.80	3.95	6.20	6.93	11.7	18.4	25.7
p, mm. (calcd.)	0.77	1.09	1.20	2.19	3.85	3.95	6.21	6.99	11.6	18.1	24.8

[a] Measurements on second sample.

TABLE V

VAPOR-PHASE DISSOCIATION OF $(CH_3)_3NBF_2CH_3$ (0.540 MILLIMOLE)

t, °C.	129.0	135.5	140.0	147.0	150.0	155.0	160.0
p, mm. (cor.)	94.87	100.0	105.25	112.12	115.04	119.92	125.56
Bulb vol., cc.	170.6	170.8	171.0	170.9	171.0	171.0	171.2
% dissociation	19.2	23.8	29.0	35.1	37.7	41.9	47.0
$K_{\text{atm.}}$ (exptl.)	0.0048	0.0080	0.01275	0.0207	0.0250	0.0335	0.0468
$K_{\text{atm.}}$ (calcd.)	0.0059	0.0093	0.01275	0.0204	0.0248	0.0341	0.0467

TABLE VI

t, °C.	25	30[a]	31	35	40	40[a]	45	50	55	55[a]	60	60[a]	65	70[a]
p, mm. (obsd.)	1.9	3.3	3.0	3.8	5.7	6.1	7.7	10.4	14.7	14.5	18.8	19.1	24.8	31.4
p, mm. (calcd.)	2.0	3.0	3.0	4.0	5.6	5.6	7.7	10.4	14.1	14.1	18.9	18.9	25.2	33.1

[a] Values from second sample.

TABLE VII

VAPOR PHASE DISSOCIATION OF $(CH_3)_3NBF(CH_3)_2$

t, °C.	74.0	77.0	80.0[a]	82.5	86.0	91.0	92.5
p, mm. (cor.)	35.40	37.00	38.50	39.65	40.45	41.70	42.00
Bulb vol., cc.	170.3	170.4	170.5	170.5	170.6	170.6	170.7
% dissociation	68.8	74.4	80.1	84.2	86.1	89.9	90.2
$K_{\text{atm.}}$ (exptl.)	0.042	0.061	0.091	0.127	0.153	0.216	0.242
$K_{\text{atm.}}$ (calcd.)	0.063	0.079	0.111	0.118	0.152	0.219	0.240

[a] After cooling and re-heating, p = 38.40 at 80°.

may be expected to become rapidly less important as the per cent. dissociation increases, and in any case the less intense dipole in $(CH_3)_3NBF_2CH_3$ should lead to an associative tendency somewhat weaker than that of $(CH_3)_3NBF_3$. It therefore seems fairly safe to assume that the equation $\log_{10} K_{\text{atm.}} = 10.315 - (5045/T)$ properly describes the dissociation, and that the corresponding free energy expression $\Delta F^0 = 23.1 - 0.0472T$ kcal. is not more than about 10% wide of the truth.

Trimethylamine Dimethylboron Fluoride.—The reaction of equimolecular samples of dimethylboron fluoride and trimethylamine was carried out at −80°, in the manometric bulb. The product was liquid at room temperature. Two samples were prepared, and the vapor–liquid equilibrium pressures were measured in the usual way. The two preparations were not exactly the same, as indicated by a slight discordance in the values at lower temperatures. Since the most probable error would be due either to a residual pressure of one component, or to a trace of trimethylboron in the original $(CH_3)_2BF$, the lower figures probably are more acceptable. The results, presented in Table VI, determine the equation $\log_{10} p_{\text{mm.}} = 9.59 - (2770/T)$, from which the check values were calculated. In this case also, the thermodynamic meaning of the results is confused by the vapor phase dissociation, and the data are presented only for descriptive purposes.

The vapor-phase dissociation of $(CH_3)_3NBF(CH_3)_2$ was first investigated by heating one of the vapor-pressure samples to several temperatures above the point of complete vaporization (range 90–155°). The results were entirely undependable, however, since a considerable part of the sample disproportionated, evidently according to the equation $2(CH_3)_3NBF(CH_3)_2 \rightarrow (CH_3)_3NB(CH_3)_3 + (CH_3)_3NBF_2CH_3$.

It was quite evident that no significant results could be obtained unless the disproportionation could be avoided, and indeed the validity of the data on vapor–liquid equilibrium would be questionable unless it could be shown that the vapor retained its identity during the measurements. Accordingly, the second vapor-pressure sample, amounting to 30.2 mg. (actual weighing) was treated with 5.7 cc. (gas at S.C.) of boron fluoride. This reacted according to the equation $BF_3 + (CH_3)_3NBF(CH_3)_2 \rightarrow (CH_3)_3NBF_3 + BF(CH_3)_2$. It was thus possible to isolate a volatile product, showing the correct vapor pressure of dimethylboron fluoride (93 mm. at −78.5°), and amounting to 5.6 cc. (theoretical, 5.69 cc.). This quantitative recovery of the original sample of $(CH_3)_2BF$ showed that no appreciable disproportionation had occurred during the measurements of vapor–liquid equilibrium pressures, and hence indicated that the vapor-phase dissociation might properly be studied at temperatures not too far above 70°.

Accordingly a small sample of $(CH_3)_3NBF(CH_3)_2$ (weighed as 19.7 mg., equivalent to 3.71 cc. of each component at standard conditions) was quantitatively condensed in the manometric bulb and its pressures were measured in the temperature range 74–92°. The dissociation constants were calculated in the same manner as for $(CH_3)_3NBF_2CH_3$. Again in this case, the lower points are not satisfactory, probably because they involve appreciable association of the complex compound itself. The data and results are presented in Table VII. If one neglects the two lowest points, the data indicate the equation $\log_{10} K_{\text{atm.}} = 10.32 - (4000/T)$, from which the check values of K were calculated. This leads to the result $\Delta F^0 = 18.3 - 0.0472T$ (kcal.), which may be taken as a very rough measure of the free energy of the process $(CH_3)_3NBF(CH_3)_2(g) \rightarrow (CH_3)_3N(g) + (CH_3)_2BF(g)$.

After these vapor-phase measurements, the bulb was cooled and the vapor tensions were checked. The results (*e. g.*, 4.8 mm. at 36°, calcd. 4.3; 10.8 at 50°, calcd. 10.4) showed that the sample had not appreciably disproportionated during the measurements.

Discussion

It appears that the substitution of one methyl for fluoride in $(CH_3)_3NBF_3$ results in an extraordinary decrease in the strength of the N→B bond, for $(CH_3)_3NBF_3$ is not measurably dissociated at 230°, whereas $(CH_3)_3NBF_2CH_3$ would be 90% dissociated under similar conditions. The substitution of a second methyl group evidently has far less effect, for the N→B bond energy of $(CH_3)_3NBF_2CH_3$ (ΔH = 23.1 kcal.) and of $(CH_3)_3NBF(CH_3)_2$ (ΔH = 18.3 kcal.) differ by scarcely five kilocalories. A third substitution seems to lower the stability by about as much again, for the rough measurements of Schlesinger, Flodin and Burg[4] on the vapor-phase dissociation of $(CH_3)_3NB(CH_3)_3$ indicate the bond energy (ΔH) to be 14 ± 1 kcal.

The contrast between $(CH_3)_3NBF_3$ and $(CH_3)_3NBF_2CH_3$ might be explained qualitatively by reference to differences of electronegativity and steric interference. The great strength of the N→B bond in the former could be attributed to the high electronegativity of fluorine, on account of which the boron atom should be unusually receptive toward electrons contributed by a base. Replacement of one fluoride by methyl should considerably decrease this effect upon the electronegativity of boron. Furthermore, the small and probably tetrahedrally-bonded F-atoms[11,12] would not exert nearly as much repulsion, against the methyl groups of the amine, as would occur if a methyl were substituted for F.

In a quantitative sense, however, this argument seems inadequate, since one would expect a second methyl substitution to have an effect nearly as large as the first. The uniform effect of the second and third substitutions is in vivid contrast to the effect of the first. The reason for this contrast might be found in the differences in the energy required to change from a planar structure[13] to tetrahedral bonding during the formation of the four different addition compounds. Since structures in which the boron atom is granted only a sextet of electrons may be regarded as improbable, the loss of resonance energy of double-bonded structures also would be a point of difference among the four compounds. These factors are at present very difficult to estimate.

Summary

The new compounds $(CH_3)_3NBF_2CH_3$ (m. p. about 35°) and $(CH_3)_3NBF(CH_3)_2$ (liquid) have been prepared and studied in regard to volatility and vapor-phase dissociation. The vapor of $(CH_3)_3NBF_3$ is considerably associated, but not dissociated below 230°. The substitution of one methyl group for fluoride in $(CH_3)_3NBF_3$ results in a large decrease in N→B bond strength, but further substitution causes relatively small decreases in the strength of that bond. Rough expressions for the free energy of dissociation of the new amine-addition compounds have been derived.

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[11] Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1939, p. 88.

[12] Bauer, Finlay and Laubengayer, THIS JOURNAL, **65**, 892 (1943).

[13] Bauer and Hastings, *ibid.*, **64**, 2691 (1942).

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY, UNIVERSITY OF CHICAGO]

Steric Factors in Quaternary Salt Formation

BY WELDON G. BROWN AND SHERMAN FRIED

The reactions of aromatic tertiary amines, in which "ortho" effects[1] appear, fall in two categories, according to whether the site of reaction is the nitrogen atom (reactions with methyl iodide, cyanogen bromide, bromoacetonitrile, etc.) or a nuclear position (coupling, nitrosation, condensations with aldehydes, etc.). The "ortho" effects in the latter type are well along toward a complete understanding, based upon the role of purely geometrical factors in a mechanism peculiar to these reactions. As yet there is no satisfactory explanation for the appearance of outwardly similar phenomena in the nucleophilic displacement reactions with alkyl halides.

As an outcome of the study[2] of a model nuclear substitution reaction showing "ortho" effects, namely, the hydrogen deuterium exchange reaction, the origin of these effects can be described with reference to the following mechanism, in which A^+ is intended to represent an electrophilic reagent.[3]

If the effective dimensions of R and R′ are such as to prevent the intermediate (I) from assuming a planar configuration, strain will arise and will be

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[1] (a) v. Braun and Kruber, *Ber.*, **46**, 3470 (1913); (b) v. Braun, **49**, 1101 (1916); (c) v. Braun and Mintz, **50**, 1651 (1917); (d) v. Braun, Arkuszewski and Kohler, **51**, 282 (1918). While there are numerous isolated observations, relating to abnormal behavior of ortho substituted tertiary amines, in the earlier literature, v. Braun seems to have been the first to recognize the generality of the phenomenon and to study it *per se*.

[2] Brown, Widiger and Letang, THIS JOURNAL, **61**, 2597 (1939).

[3] In the hydrogen–deuterium exchange reaction, A^+ is a deuteroacid. As applied to the coupling reaction, A^+ is diazonium ion, and the mechanism becomes identical with that written by Dilthey and Blankenburg [*Ann.*, **142**, 185 (1935)], which has been supported recently by Wistar and Bartlett [THIS JOURNAL, **63**, 413 (1941)] and by Hauser and Breslow [*ibid.*, **63**, 418 (1941)].