

[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY, CORNELL UNIVERSITY]

Energetics of the Boranes. I. The Heats of Reaction of Diborane with the Methylamines, and of Tetramethyldiborane with Trimethylamine; the Dissociation Energy of Diborane¹

By R. E. MCCOY² AND S. H. BAUER

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A thermochemical extrapolation procedure has been utilized in estimating the heat of dissociation for $B_2H_6(g) = 2BH_3(g)$. The necessary data were obtained by allowing gaseous methylamines to react with diborane and with tetramethyldiborane in an isothermal calorimeter of the Ginnings type, which has been constructed for this purpose; precision of the measurements was estimated to be about 0.1 cal. The $B \begin{array}{c} \text{H} \\ \diagdown \quad \diagup \\ \text{H} \end{array} B$ bridge breaking energy for diborane and of its alkyl substituted homologs are compared. The heat of formation of BH_3 has been deduced, and a value is given for the B-H average bond dissociation energy. The relative instability of the hydrides of boron is not due to low bond dissociation energies. One should consider them as being highly reactive due to the presence of low energy barriers for dissociation to give highly reactive units, comparable in the hydrocarbon system to those cases where a carbonium ion is produced readily.

Introduction

At the time when this investigation was initiated no reliable estimate was available of the energy of dissociation of diborane-6³ to borane. Only widely separated limits of 13.6^{4a} and about 50^{4b} kcal. per mole had been established. Attempts to detect borane in diborane by pressure measurements⁵ and observation of spectra⁶ had failed, but considerable evidence was available that borane is an intermediate in a variety of chemical reactions.⁷

The major objective of this research was to obtain experimental data from which a close estimate of the heat of dissociation of diborane might be deduced. The heats of reaction of diborane and tetramethyldiborane with trimethylamine were selected as the new measurements to be made. These and the heats of reaction of diborane with methylamine and dimethylamine were measured calorimetrically and used in conjunction with the published heats of reaction of boron trimethyl with ammonia and the methylamines⁸ to make the necessary estimation. The procedure used might be described as a "thermochemical interpolation."

Experimental

Equipment.—The calorimeter that was used is similar to one described by Ginnings and co-workers.⁹ The associated gas handling apparatus is sketched in Fig. 1; the attached vacuum system permits use of the calorimeter to measure heats of reactions between gases. When set up for negligible heat leak, the precision of the calorimeter for the measurement of heat increments is 0.1 cal. This was checked

by determining the integral heat capacity of a piece of copper of known weight, initially cooled to a measured temperature. In most of our work there was a small, nearly constant heat leak, which might introduce an error of similar magnitude. Except in the measurements with tetramethyldiborane the errors in heat leak are small compared to the normal errors in measuring the amounts of gases employed.

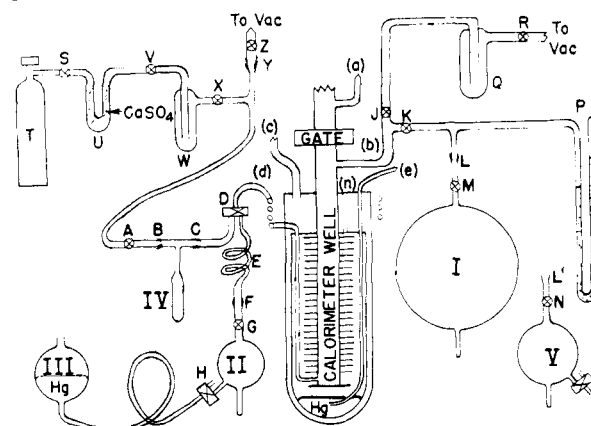


Fig. 1.—Associated vacuum line.

Procedure for the Reaction of Diborane with Amines.—A quantity of amine (purchased from Matheson) adequate for several determinations was purified by distillation from sodium and by freezing and pumping in the vacuum system, condensed in bulb I, and stored in the position shown. Before the day of a run 5 ml. of mercury was placed in tube IV; the calorimeter system and the bulb were thoroughly evacuated. On the day of the run a convenient amount of diborane (obtained from General Electric Company Research Laboratory) was repurified in the vacuum system by distillation from a trap maintained at the melting point of technical grade *n*-propyl alcohol and its temperature and pressure were measured in a known volume. It was then condensed in bulb II, which was transferred to the position shown. The joint was waxed and the bulb was supported to permit filling it with mercury later. The joint (EF) was then evacuated. Meanwhile, the diborane was kept condensed with liquid nitrogen.

Tube IV (pivoted along BC) was inverted and the line from tank T was evacuated. About one atmosphere of dry nitrogen was admitted to the bulb, forcing the mercury against stopcock D. Stopcocks D and J were closed and the amine was admitted to the manometer and calorimeter at a pressure well below its vapor pressure at 0° and such that the quantity in the calorimeter was about equivalent to the diborane used. Ice was piled high about the calorimeter to bring the entire region to 0° and to minimize the heat leak. After the amine had come to temperature equilibrium the pressure was measured and stopcock K was

(1) From a thesis presented to the faculty of the Graduate School of Cornell University by Robert E. McCoy in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1952. Presented in part at the 122nd Meeting of the A.C.S. at Atlantic City, N. J., Sept. 18, 1952.

(2) Atomic Energy Commission Fellow of the National Research Council, 1949–1952.

(3) The Shaeffer-Wartek, system of nomenclature has been used in this paper.

(4) (a) R. P. Bell and H. C. Longuet-Higgins, *Proc. Roy. Soc. (London)*, **A183**, 357 (1945); (b) R. P. Clarke and R. N. Pease, *THIS JOURNAL*, **73**, 2132 (1951).

(5) A. Stock and E. Kuss, *Ber.*, **56B**, 789 (1923).

(6) G. C. Pimentel and K. S. Pitzer, *J. Chem. Phys.*, **17**, 882 (1949).

(7) Some of this evidence is summarized by H. I. Schlesinger and A. B. Burg, *Chem. Revs.*, **31**, 1 (1942).

(8) H. C. Brown, H. Bartholomay and M. D. Taylor, *THIS JOURNAL*, **66**, 435 (1944).

(9) (a) D. C. Ginnings, T. B. Douglas and A. F. Ball, *J. Research Natl. Bur. Standards*, **45**, 23 (1950); (b) D. C. Ginnings and R. J. Corruccini, *ibid.*, **38**, 583 (1947).

closed. Stopcock D was opened to tube IV allowing nitrogen to push the mercury into the calorimeter and sweep out the inlet tube; this confined the amine to the calorimeter. The heat leak was checked for 15–30 min. using a weighed bottle of mercury in the measuring system [exit e]. Near the end of this check the diborane was allowed to vaporize.

On completion of the heat leak check, stopcocks H and G were opened and D slightly opened so that the mercury slowly pushed the diborane into the calorimeter. Slow introduction allowed the reaction to occur at the bottom of the calorimeter and avoided local overheating and possible side reactions. A new weighed bottle of mercury was used to determine the amount of mercury withdrawn into the calorimeter and hence the heat evolved in the reaction. When all the diborane had been pushed through stopcock D, the stopcock was turned to allow the nitrogen in tube IV to flush the residual diborane into the calorimeter. After the calorimeter had come to equilibrium the heat leak was checked again. The heat of reaction was calculated from the heat equivalent of the mercury intake and the measured volumes of the reactants. In the case of methylamine and dimethylamine a small correction for the heat of secondary reactions had to be added.

Reaction of Tetramethyldiborane and Trimethylamine.—Boron trimethyl was prepared by the reaction of boron trifluoride with methyl Grignard reagent in dibutyl ether. It was purified by fractional vaporization and condensation, retaining the fraction condensed at the freezing point of *n*-propyl alcohol but volatile at Dry Ice temperature. Purification was repeated until the vapor pressure at the Dry Ice point was constant at 29.5 mm. for all fractions regardless of the volume of the vapor.

Tetramethyldiborane was then prepared by the method of Schlesinger and Walker.¹⁰ A chloroform slush bath (approx. -64°) was substituted for the -70° temperature in the preliminary purification, and great care was taken to obtain slow evaporation of the mixture. The cited final purification procedure could not be duplicated, probably because of the greater capacity and efficiency of the vacuum pump and train used here. Consequently, the preliminary purification was repeated several times. Tetramethyldiborane with a constant vapor pressure of 49 mm. at 0° was obtained. It was kept condensed at liquid nitrogen temperature until used, to prevent slow disproportionation, which occurs even at Dry Ice temperature.

The low vapor pressure of tetramethyldiborane at 0° prohibits its introduction as a gas in the manner used for diborane. Therefore, the amine was placed in bulb II and the bulb containing purified tetramethyldiborane was attached at joint L (Fig. 1). Because of the small amount of tetramethyldiborane available, that part of the vacuum line which was to be exposed to this material was previously conditioned with boron trimethyl. After standing for some time, the boron trimethyl was trapped out and any gaseous decomposition products were evacuated thoroughly. Shortly before the reaction, tetramethyldiborane was allowed to vaporize into the calorimeter until the pressure was about 45 mm. When it had come to temperature equilibrium the pressure was measured and the calorimeter was isolated. The rest of the procedure was similar to that for diborane.

Evaluation of Secondary Reactions of Methylamine-Borane and Dimethylamine-Borane.—The products of the reactions of trimethylamine with diborane¹¹ and tetramethyldiborane¹² are stable and undissociated in the vapor phase at ordinary temperatures. In contrast dimethylamine-borane and methylamine-borane decompose slowly with evolution of hydrogen even at 0° . To determine the extent of decomposition during measurement of the heat of reaction, a small amount of carbon dioxide was substituted for nitrogen as the inert gas in the regular procedure. Condensation of other gases with liquid nitrogen permitted measurement of the hydrogen evolved. The results of several tests indi-

cate about 5% of the product decomposed initially due to local heating during reaction. Decomposition was much slower after the product cooled to 0° . Dimethylamine-borane decomposes according to the equation



followed by dimerization of the dehydrogenation product.¹³ Since the hydrogen evolution of methylamine-borane is almost identical to that of the dimethyl compound, it must decompose similarly with little contribution from further dehydrogenation.

The ΔH° of dehydrogenation is assumed to be about two thirds that of propane, 30 kcal.¹⁴ The ΔH° of dimerization of Me_2NBH_2 is approximately -10 kcal. per mole of monomer.¹⁵ Therefore the over-all ΔH° is about 10 kcal. The correction for 5% decomposition is 0.6 kcal. to be added to the measured value.

Conversion of Results to Gas Phase.—The products of the reactions studied are all solids or liquids. To permit valid comparison of these and other reactions and to facilitate the desired calculations, the results were converted to the gas phase by use of appropriate heats of sublimation and vaporization. The vapor pressure of trimethylamine-borane at 0° is less than 0.1 mm., and the heat of sublimation has been calculated to be 13.99 kcal./mole.¹¹ The heat of vaporization of trimethylamine-dimethylborane is 9.61 kcal. and the vapor pressure at 0° is 1.0 mm.¹² This vapor pressure is not negligible compared to the small amount of material used. In calculating the heat of reaction to the liquid product a correction was made for the heat of vaporization of the uncondensed vapor. The heats of sublimation of dimethylamine-borane and methylamine-borane have not been determined; their tendency to dehydrogenate when heated prevents measurement by the usual technique. It is expected that these values do not differ greatly from that of trimethylamine-borane. For comparison, the values for trimethylamine-borane,¹¹ trimethylamine-methylborane and trimethylamine-dimethylborane¹² decrease in steps of about 0.2 kcal. The desired values are not readily predicted from those just given, therefore a value of 14.0 kcal. was assumed in both cases.

The deduced enthalpy increments are given in Table I. These are the averages of three determinations except for reaction (4), where only two runs were made. The average deviation in the measured value is given. If analysis of possible errors suggests a greater uncertainty, an estimate of the latter is given for the gas phase reaction. Uncertainties as to the extent and effect of secondary reactions, and the value of the heat of sublimation, led to a larger estimated error for reaction (2). Possible errors of 1–2% in pressure measurement and of 1% in measuring the small quantity of heat involved, plus possible deviation from ideal behavior of tetramethyldiborane vapor near its vapor pressure, are factors in the uncertainty given for reaction

(13) E. Wiberg, A. Bolz and P. Buchheit, *Z. anorg. Chem.*, **256**, 285 (1948).

(14) G. E. K. Branch and M. Calvin, "The Theory of Organic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1941, p. 275.

(15) A. B. Burg and C. L. Randolph, *THIS JOURNAL*, **73**, 953 (1951).

(10) H. I. Schlesinger and A. O. Walker, *THIS JOURNAL*, **57**, 621 (1935).

(11) A. B. Burg and H. I. Schlesinger, *ibid.*, **59**, 780 (1937).

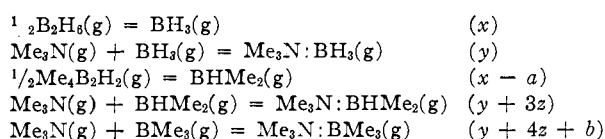
(12) H. I. Schlesinger, N. W. Flodin and A. B. Burg, *ibid.*, **61**, 1078 (1939).

TABLE I

| | $-\Delta H_{273}^{\circ}(\text{to s or l})$ | $-\Delta H_{273}^{\circ}(\text{to g})$ |
|---|---|--|
| (1) $\text{Me}_3\text{N}(\text{g}) + \frac{1}{2}\text{B}_2\text{H}_6(\text{g}) = \text{Me}_3\text{N}:\text{BH}_3(\text{s})$ | 31.27 ± 0.15 | 17.3 ± 0.15 |
| (2) $\text{Me}_2\text{HN}(\text{g}) + \frac{1}{2}\text{B}_2\text{H}_6(\text{g}) = \text{Me}_2\text{HN}:\text{BH}_3(\text{s})$ | $32.49 \pm .66$ | $18.9 \pm .7$ |
| (3) $\text{MeH}_2\text{N}(\text{g}) + \frac{1}{2}\text{B}_2\text{H}_6(\text{g}) = \text{MeH}_2\text{N}:\text{BH}_3(\text{s})$ | $31.06 \pm .29$ | $17.5 \pm .5$ |
| (4) $\text{Me}_3\text{N}(\text{g}) + \frac{1}{2}\text{Me}_4\text{B}_2\text{H}_2(\text{g}) = \text{Me}_3\text{N}:\text{BHMMe}_2(\text{l})$ | $20.62 \pm .20$ | $11.0 \pm .6$ |
| (5) $\text{Me}_3\text{N}(\text{g}) + \text{BMe}_3(\text{g}) = \text{Me}_3\text{N}:\text{BMe}_3(\text{g})$ | | 17.6 |

(4). The value given by Brown and co-workers⁸ for reaction (5) at 100° has been included in the table. The error involved in using ΔH_{373}° for ΔH_{273}° is probably no greater than the uncertainty in the value for reaction (4).

Interpretation of the Results.—The specific enthalpy increments we wish to evaluate are



The necessary five unknowns were introduced in the manner indicated to call attention to their physical interpretations. Since only three thermochemically independent measurements are available, two additional pieces of information must be obtained to permit solution of the set of simultaneous equations. The significance of x and y is clear; $2a$ is the decrement in the dissociation energy introduced by substitution of four methyl groups for the terminal hydrogen atoms in diborane. Calculations based on rough equilibrium data for disproportionation reactions among the substituted methylboranes,¹⁰ give $2a = 3.5$ kcal. This value will be justified below in the section on *bridge breaking energies*.

The two variables z and b are inductive and steric factors, respectively. To justify the coefficients with which the z 's were inserted, and for accepting the value for $b = 3.2$ kcal., the reader is referred to the section on *acid-base strengths*. Accepting these for the present, one may express the three experimentally determined thermochemical values as

$$\begin{aligned} x + y &= -17.3 \\ x + y + 3z - a &= -11.0 \\ y + 4z + b &= -17.6 \end{aligned}$$

which give on solution

$$\begin{aligned} x &= 14.2 \text{ kcal.} & x - a &= 12.5 \text{ kcal.} \\ y &= -31.5 \text{ kcal.} & y + 3z &= -23.4 \text{ kcal.} \\ z &= 2.7 \text{ kcal.} & y + 4z + b &= -17.6 \text{ kcal.} \end{aligned}$$

The magnitude of y is a measure of the relative acid strength of BH_3 (NMe_3 as reference base). For comparison we estimate the heat of reaction between trimethylamine and BF_3 to produce the *gaseous* product to be about 26.5 kcal., while that for trimethylamine with BCl_3 (*gaseous* product) to be about 30 kcal.

The value for the bridge dissociation energy in diborane is 28.4 kcal. per mole, with an estimated error ± 2 kcal. This is within the limits cited in the Introduction. One may argue that since $\Delta S_{\text{diss}}^{\circ}$ can be computed with sufficient certainty,¹⁶ the fact that no appreciable dissociation occurs in di-

borane at a temperature of 400°K., in that no appreciable pressure increase was detected⁵ except that due to a slight pyrolysis, provides a lower limit to $\Delta H_{\text{diss}}^{\circ}$.

$$\begin{aligned} \frac{p_{\text{BH}_3}}{p_{\text{B}_2\text{H}_6}} &= \left[\frac{K_p}{p_{\text{B}_2\text{H}_6}} \right]^{1/2} < 10^{-3}; p_{\text{B}_2\text{H}_6} = 1 \text{ atm.} \\ \log_{10} K_p &= \left[7.478 - \frac{0.1285}{T} \Delta H_{\text{diss}}^{\circ} \right] < -6.0 \\ \Delta H_{\text{diss}}^{\circ} &> 25 \text{ kcal. mole}^{-1} \end{aligned}$$

Further confirmatory values which include both lower and upper limits follow from about seven gas kinetic studies. These have been assembled and analyzed and will be presented in paper II of this series. The equilibrium constant for dissociation is given by

$$\log_{10} K_{p(\text{atm})} = 7.478 - 6205/T$$

Upon combining the above values for the heat of dissociation with the accepted value for the heat of formation of diborane^{16,17} one obtains for BH_3

$$\begin{aligned} \Delta H_f^{\circ}(300^{\circ}\text{K.}) &= 18 \pm 1 \text{ kcal.} \\ S^{\circ}(300^{\circ}\text{K.})_{\text{ideal gas}} &= 44.9 \text{ e.u.} \end{aligned}$$

One may now deduce an average bond dissociation energy for B-H, taking 140.9 kcal.¹⁸ for the molar heat of sublimation of boron; it is 93.1 kcal. For comparison, the *abde* for C-H in methane is 99.5 kcal. ($\Delta H_{\text{sub}}(\text{C}) = -171.9$ kcal./mole) and that for N-H in ammonia is 99.3 kcal. ($D_{\text{N}_3} = 224.9$ kcal.¹⁹). Clearly, one should not consider the boron-hydrogen bond as being particularly "weak." With the above magnitude of the average bond dissociation energy for B-H, assuming that the hybridization on boron is sp^2 , one may deduce a value for a similar trigonal B-B bond, by using Pauling's relation: $D_{\text{B-H}} = \frac{1}{2}(D_{\text{B-B}} + D_{\text{H-H}}) + 23.06(x_{\text{H}} - x_{\text{B}})$.² This gives $D_{\text{B-B}}(\text{sp}^2) = 81$ kcal., and is to be compared with the value for an average B-B bond for hexa-ligandated boron as deduced from its heat of sublimation.¹⁸ Since in a unit cell in the element there are 50 atoms making a total of 148 bonds, one obtains an average value of 47.6 kcal. per bond; however, since there are only 150 valence electrons per unit cell the average dissociation energy for unit bond order is $(47.6 \times 75)/148 \cong 96.5$ kcal.

Bridge Breaking Energies.—Schlesinger and Walker¹⁰ have quoted results of three equilibration experiments between diborane and boron trimethyl. After mixing the two gases in three different ratios and allowing them to sit for many hours so that the systems reached equilibrium at room

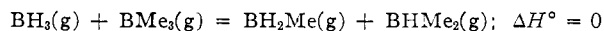
(17) E. J. Prosen, W. H. Johnson and F. A. Yenchis, Private Communication, and NBS report to ONR (September 1948).

(18) A. W. Searcy and C. E. Myers, Purdue University, Contract No. N 7, ONR 394/12. TR 6 (1953).

(19) J. M. Hendrie, *J. Chem. Phys.*, **22**, 1503 (1954).

(16) Allan Shepp and S. H. Bauer, *THIS JOURNAL*, **76**, 265 (1954).

temperature, they analyzed the mixtures for products. In one experiment they started with a 1:1 ratio (approximately $1/2$ atmosphere for each constituent) and found that the final mixture consisted of 8.1% mono:81.6% di (unsymmetric); 8.0% tri; and 2.3% tetramethyldiborane. The system may be described in terms of three simultaneous reactions and the data may be reduced to relative equilibrium constants, as are formulated in Table II. Their data for the other two experiments were not as complete as those for the one quoted, but these are in rough agreement with the values cited. The computed equilibrium constants given in the last column of the table are based on the assumption



and the values listed in Table III. It is clear that whereas the methyl substituted diboranes should show no tendency to disproportionate into the terminal products, as per the last equation in Table II, their interconversions should be extensive at room temperature.

TABLE II
(All substances in gaseous state; 300°K.).

| | $K_{\text{exp.}}$ (ref. 8) | $K_{\text{comp.}}$ |
|--|-------------------------------|----------------------|
| $2\text{B}_2\text{H}_6 = \text{B}_2\text{H}_6 + \text{B}_2\text{H}_4\text{Me}_2$ (unsym.) | 2.8 | 3.1 |
| $3\text{B}_2\text{H}_6\text{Me}_1$ (unsym) = $\text{B}_2\text{H}_6 + 2\text{B}_2\text{H}_3\text{Me}_2$ | 2.7×10^{-4} | 5.2×10^{-4} |
| $4\text{B}_2\text{H}_6\text{Me}_2 = \text{B}_2\text{H}_6 + 3\text{B}_2\text{H}_2\text{Me}_3$ | 6.7×10^{-3} | 3.5×10^{-3} |
| $6\text{B}_2\text{H}_6\text{Me}_3 = 5\text{B}_2\text{H}_6 + 2\text{BMe}_3$ | ... | $\sim 10^{-12}$ |

TABLE III

| Compound | Bridge breaking energy, kcal. | $S^\circ(300)$, e.u. ideal gas | Ref. |
|--|-------------------------------|---------------------------------|------|
| B_2H_6 | 28.5 | 55.32 | 16 |
| $\text{B}_2\text{H}_5\text{Me}$ | 28.0 | 65.7 | 20 |
| $\text{B}_2\text{H}_4\text{Me}_2$ (unsym.) | 28.5 | 75.0 | 20 |
| $\text{B}_2\text{H}_3\text{Me}_3$ | 26.5 | 84.0 | 20 |
| $\text{B}_2\text{H}_2\text{Me}_4$ | 25.0 | 92.6 | 20 |
| B_2HMe_5 | <5 | .. | .. |
| BMe_3 | .. | 75.1 | 20 |

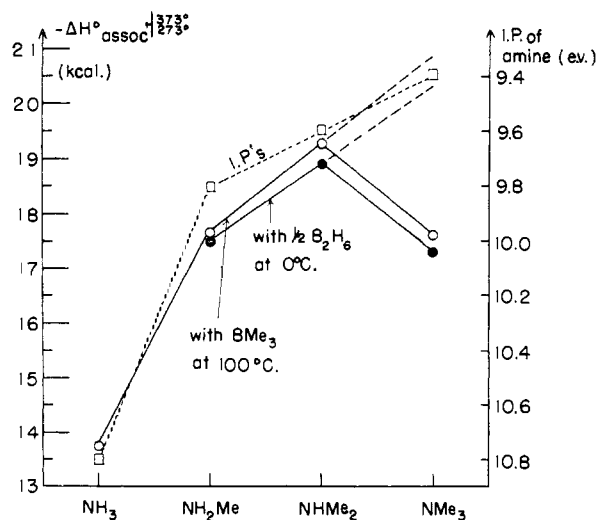


Fig. 2.—Effect of methyl substitution on basicity of amines.

(20) Values interpolated from a plot of $S^\circ(300)$, ideal gas, versus the logarithm of the molecular weight. For comparison, a parallel plot was made of the tabulated entropies of the structurally analogous branched chain alkenes and alkanes.

Acid-Base Strengths.—It has been originally pointed out by Lewis²¹ and amply demonstrated in later work that one may measure the *relative* acid or base strengths of a sequence by allowing each member to react with a selected reference base or acid, respectively, and determining the free energy release for the association. This order may change when another reference compound is utilized. However, there are good theoretical reasons why the enthalpy rather than the free energy should be the measure. Further, one may consider the ionization potential of the base, for the removal of an electron which is in a p-orbital, as an *absolute* measure of the ease for giving up electrons (base strength); but this value is modified by polarizabilities and steric factors arising as a consequence of donor-acceptor compound formation. Similarly, the electron affinity of an acid may be considered to be an absolute measure of its strength, again modified by similar factors when the compound is formed.²² The inductive influence when methyl groups are substituted for hydrogen atoms clearly shows up as a decrease in ionization potential for the NH_3 , OH_2 , and SH_2 sequences.²³ The ionization potentials for the amines are graphed in Fig. 2. It appears that the first methyl group is about five times as effective in releasing electrons as are the subsequent groups; thenceforth, the effect is strictly linear.

In striking parallel are the heats released when amines are allowed to react with boron trimethyl as the reference acid⁸ and with one-half mole of diborane as a reference acid (our data); cf. Fig. 2. The inductive effect again appears with the first methyl introduced being about twice as effective as the subsequent ones. We now wish to argue that the inductive effect in methyl substitution follows exactly the same pattern in *decreasing acid strength* as it does in *increasing base strength*, so that the sequence we shall accept is $\text{BH}_3 > \text{BH}_2\text{Me} > \text{BHMe}_2 > \text{BMe}_3$. Because of the symmetry between the series $\text{Me}_3\text{N}:\text{BH}_3 - n\text{Me}_n$ and $\text{Me}_n\text{H}_3 - n\text{N}:\text{BMe}_3$, this assumption does not depend on whether B-strain⁸ or F-strain²⁴ is involved. Quantitatively we shall write as equivalent: $\text{BH}_3 \sim \text{BH}_2\text{Me} + 2z \sim \text{BHMe}_2 + 3z \sim \text{BMe}_3 + 4z$. If other factors did not enter the enthalpy of association of trimethylamine with boron trimethyl would be the extrapolated value of -20.9 kcal. and that for trimethylamine with $1/2 \text{B}_2\text{H}_6$ would be -20.3 kcal.; cf. Fig. 2. The lower values which have been observed are to be interpreted that when six bulky groups must be placed about N-B steric repulsion lowers the stability of the compound by about 3.2 kcal. This then is the value for b which was used above.

This research was supported in part by the Office Naval Research.

Errata to Tables I and II.¹⁶—Regrettably several typographical and computational errors appeared in the above paper. Revised values numbered to

(21) G. N. Lewis, *J. Frank. Inst.*, **226**, 293 (1938).

(22) R. S. Mulliken, *THIS JOURNAL*, **74**, 811 (1952); *J. chim. phys.*, **51**, 341 (1954).

(23) W. C. Price, *Chem. Revs.*, **41**, 257 (1947).

(24) R. Spitzer and K. S. Pitzer, *THIS JOURNAL*, **70**, 1261 (1948).

TABLE IV
THERMODYNAMIC DATA FOR HOMOGENEOUS GAS PHASE ASSOCIATIONS^a
 ΔS^0 in e.u. at 300° and one atmosphere (ideal gas state); ΔH^0 in kcal./mole.

| | $\Delta S^0_{\text{comp.}}$ | $\Delta S^0_{\text{meas.}}$ | ΔH^0 | Ref. |
|--|-----------------------------|-----------------------------|----------------------|------|
| (3) $\text{BH}_3 + \text{BH}_3 = \text{B}_2\text{H}_6$ | -34.22 | | -28.5 | b |
| $\text{BHMe}_2 + \text{BHMe}_2 = \text{B}_2\text{H}_2\text{Me}_4$ | | | -25.0 | b |
| (4) $\text{CO} + \text{BH}_3 = \text{OC}:\text{BH}_3$ | -33.17 | | -18.8 | b |
| (5) $\text{BF}_3 + \text{CO} = \text{OC}:\text{BF}_3$ | -36.0 | | (-14) ^c | 16 |
| (6) $\text{CO} + \frac{1}{2}\text{B}_2\text{H}_6 = \text{OC}:\text{BH}_3$ | -16.05 | | -4.57 | 25 |
| (7) $\text{Me}_3\text{N} + \text{BH}_3 = \text{Me}_3\text{N}:\text{BH}_3$ | -37.80 | | -31.5 | b |
| (8) $\text{Me}_3\text{N} + \frac{1}{2}\text{B}_2\text{H}_6 = \text{Me}_3\text{N}:\text{BH}_3$ | -20.69 | | -17.3 | b |
| $\text{Me}_3\text{N} + \text{BHMe}_2 = \text{Me}_3\text{N}:\text{BHMe}_2$ | (-44) ^c | | -23.4 | b |
| $\text{Me}_3\text{N} + \frac{1}{2}\text{B}_2\text{H}_2\text{Me}_4 = \text{Me}_3\text{N}:\text{BHMe}_2$ | | | -11.0 | b |
| $\text{Me}_3\text{N} + \text{BMe}_3 = \text{Me}_3\text{N}:\text{BMe}_3$ | | -45.7 | -17.6 | 8 |
| $\text{Me}_3\text{N} + \text{BMe}_2\text{F} = \text{Me}_3\text{N}:\text{BMe}_2\text{F}$ | | -47.2 | ~-20.5 | 26 |
| $\text{Me}_3\text{N} + \text{BMeF}_2 = \text{Me}_3\text{N}:\text{BMeF}_2$ | | -47.2 | -23.1 | 26 |
| (9) $\text{Me}_3\text{N} + \text{BF}_3 = \text{Me}_3\text{N}:\text{BF}_3$ | -46.1 | | -26.6 | 27 |
| $\text{Me}_3\text{N} + \text{BCl}_3 = \text{Me}_3\text{N}:\text{BCl}_3$ | | | (-30.5) ^c | |

^a With respect to Me_3N as a reference base, BF_3 appears to be "weaker" than BH_3 by about 5 kcal., as an acid. Reaction (5) is strictly hypothetical; $\text{OC}:\text{BF}_3$ has not yet been prepared although serious attempts to do so have been made. We doubt that direct addition can lead to this substance. ^b Data in this paper. ^c Estimated values.

correspond to the equations as originally designated are given in Table IV, along with other closely related values which are of interest.

(25) A. B. Burg, *ibid.*, **74**, 3482 (1952).

(26) A. B. Burg and A. A. Green, *ibid.*, **65**, 1838 (1943).

(27) Unpublished data by McCoy and Bauer.

ITHACA, N. Y.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF TENNESSEE]

Some Reactions of Monoammonia-boron Trifluoride with Solutions of Alkali Metals in Ammonia

BY W. J. MCDOWELL¹ AND C. W. KEENAN

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The reactions of the alkali metals, lithium, sodium, potassium and cesium, with liquid ammonia solutions of $\text{BF}_3\cdot\text{NH}_3$ have been studied. Differences in the stoichiometry of reaction for these metals have been observed; the mole ratio of metal: $\text{BF}_3\cdot\text{NH}_3$ is 3.0 for lithium, 2.5 for sodium and 1.0 for both potassium and cesium. The products of the reaction of $\text{BF}_3\cdot\text{NH}_3$ with potassium have been studied and proposals have been made as to the nature of the products of the reactions with the other metals.

Introduction

This study was undertaken to extend the knowledge of the chemistry of boron compounds in liquid ammonia. Kraus and Brown² have described the reaction between sodium and $\text{BF}_3\cdot\text{NH}_3$ in this solvent. They found that hydrogen was evolved in stages and interpreted this as indicating that all the fluoride ligands are not solvolyzed with equal ease. Further, from the fact that the solvolysis of the ethylamine derivative of BF_3 may go to completion, as indicated by the reaction of lithium with a solution of BF_3 in ethylamine, they concluded that a liquid ammonia solution of $\text{BF}_3\cdot\text{NH}_3$ should be completely ammonolyzed.

Our investigation has revealed some unexpected and interesting chemical properties of the $\text{BF}_3\cdot\text{NH}_3$ -liquid ammonia system.

Experimental

Apparatus.—Most of the reactions in liquid ammonia were carried out in an apparatus similar to one which has been described.³

All of the reaction products were handled in a dry box filled with anhydrous, oxygen-free nitrogen.

X-Ray powder diffraction photographs were made of several of the products with a Model 795 Picker-Waite diffraction unit. The samples were enclosed in thin-walled Pyrex capillaries and exposed in a 70 mm. camera to radiation from a tube equipped with a copper target and a nickel filter. An accelerating voltage of 45 kv., a filament current of 9 ma., and an exposure time of 1 hr. were used for all samples.

Reagents.—The ammonia used in all quantitative reactions was purified from commercial material (99.9%) by distilling and storing in small cylinders containing sodium amide.

The $\text{BF}_3\cdot\text{NH}_3$ was prepared by the addition of ammonia to boron trifluoride etherate as described by Kraus and Brown.² The white precipitate was allowed to settle and the excess ether removed by decantation. The product was washed twice with fresh ether and then freed of ether by evacuation.

Anal. Calcd. for $\text{BF}_3\cdot\text{NH}_3$: B, 12.8; F, 67.2; N, 16.5. Found: B, 12.4; F, 67.9; N, 16.4.

All other chemicals used were reagent grade except the cesium which was distilled from C.P. material.

The Analysis of Boron Compounds Containing Fluorine.—The method of Pflaum and Wenzke,⁴ modified to exclude the sodium peroxide fusion, was used to analyze compounds containing boron and fluorine.

(1) Oak Ridge National Laboratory, Oak Ridge, Tennessee.

(2) C. A. Kraus and E. H. Brown, *THIS JOURNAL*, **51**, 2690 (1929).

(3) G. W. Watt and C. W. Keenan, *ibid.*, **71**, 3833 (1949).

(4) D. J. Pflaum and H. H. Wenzke, *Ind. Eng. Chem., Anal. Ed.*, **4**, 392 (1932).