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THE CHEMISTRY OF BORON HYDRIDES AND RELATED HYDRIDES

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ABSTRACT

Additional data obtained on the product from the reaction of $B_4H_{10} \cdot 2NH_3$ and HF suggest that the new compound may be a fluoroborate of the cation $H_2B(NH_3)_2^+$ rather than a fluoride. New data and more careful methods of data reduction give values of 18.8, 18.5, and 13.6 kcal/mole for the heats of sublimation of $(CH_3)NE_2BH_3$, $(CH_3)_2NHBH_3$, and $(CH_3)_3NBH_3$, respectively. Dipole-moment values for the amine-boranes in other solvents are being obtained. A Raman spectral study of the amine-boranes is described. PF_3BH_3 reacts with ammonia to give $(NH_2)_3PBH_3$. Failure of H_3NBH_3 to react with PF_3 and ammonia under comparable conditions argues against a reaction mechanism involving replacement of F_3P by NH_3 in the complex. Preliminary X-ray structural data on $(NH_2)_3PBH_3$ have been obtained. Infrared and Raman spectra of $H_3NB_3H_7$ and $Me_3NB_3H_7$ have been obtained as part of a spectral study. Preliminary X-ray crystallographic data on $B_4H_{10} \cdot 2NH_3$ are reported.

Tetraborane reacts with KBH_4 by a symmetrical cleavage process and with KOH and $KOCH_3$ by nonsymmetrical cleavage processes to give KB_3H_8 .

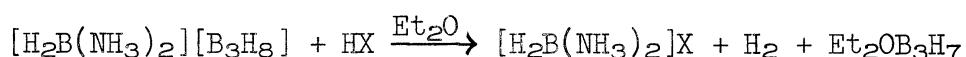
PF_3 reacts with Al_2Me_6 but the products formed have not yet been identified.

$H_3Al(NME_3)_2$ has a dipole moment of 1.3D in benzene solution. Preliminary X-ray crystallographic data are presented.

I. THE CHEMISTRY AND STRUCTURE OF THE
DIAMMONIATE OF DIBORANE AND ITS DERIVATIVES

A. BACKGROUND

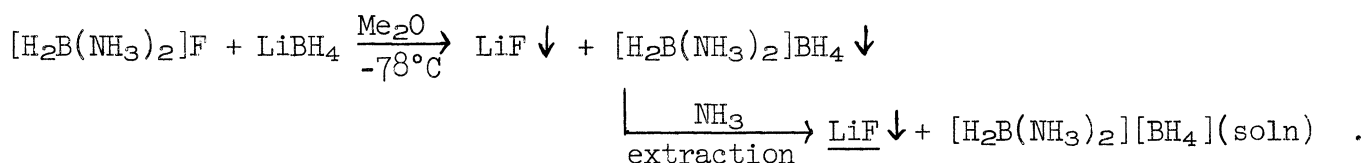
The type reaction:



has been used to prepare the chloride, bromide, and iodide salts of $[\text{H}_2\text{B}(\text{NH}_3)_2]^+$. An extension of the reaction to prepare the fluoride salt, $[\text{H}_2\text{B}(\text{NH}_3)_2]\text{F}$, appeared to be obvious and routine, but unexpected difficulties have arisen in carrying out the reaction and characterizing the product obtained. In previous reports analytical problems were mentioned and it was reported that molecular weight values of the supposed $[\text{H}_2\text{B}(\text{NH}_3)_2]\text{F}$ were near 120 or roughly twice the expected value of 66. Attempts to obtain a more definitive characterization of the compound have been continued.

B. FURTHER STUDIES OF THE COMPOUND RESULTING FROM THE REACTION BETWEEN $\text{B}_4\text{H}_{10} \cdot 2\text{NH}_3$ AND HF

In an earlier report the reaction of $\text{B}_4\text{H}_{10} \cdot 2\text{NH}_3$ and HF in diethyl ether at -78°C was described. The compound formed was tentatively identified as $[\text{H}_2\text{B}(\text{NH}_3)_2]\text{F}$ on the basis of the reaction:



The solid $\text{B}_2\text{H}_6 \cdot 2\text{NH}_3$ and LiF were identified by their X-ray powder patterns. The complete characterization of the compound was complicated by analytical problems. The molecular weight value as measured by vapor-pressure depression of an Me_2O solution was around 120 as compared to a theoretical value of 66. The best new values for the percentage of ammonia are 25.2 and 26.2 as compared to 51.5 expected for $[\text{H}_2\text{B}(\text{NH}_3)_2]\text{F}$. The observed value for hydrogen is 1.76% as compared to an expected value of 3.04%. For boron the value is 17.3 as compared to 16.4 expected. The data taken together indicate that the characterization as $[\text{H}_2\text{B}(\text{NH}_3)_2]\text{F}$ is probably incorrect. An attractive alternative possibility for the formula of the compound is $[\text{H}_2\text{B}(\text{NH}_3)_2]\text{BF}_4$. Theoretical values for this compound would be: Mol wt = 134, % NH_3 = 25.3, H^- = 1.49, B = 16.1. The results are still inconclu-

sive, but all data are reasonably consistent with the fluoroborate interpretation. An authentic fluoroborate sample will be made for comparison. It is interesting to note that the reaction of $B_4H_{10} \cdot 2NH_3$ with HF is completely different from the reaction of the other hydrohalogen acids and $B_4H_{10} \cdot 2NH_3$.

C. ATTEMPTS TO SYNTHESIZE $K_2[BH_2NHCH_3]$

1. Earlier arguments arising from the reaction between H_2BNH_2 and NH_3 in the presence of Na led to the suggestion from this laboratory that a compound $Na_2[H_2BNH_2]$ might be formed as an intermediate. It was suggested that a related compound $K_2[H_2BNHCH_3]$ might even be prepared as a stable compound by the reaction between metallic potassium in liquid ammonia and $[H_2BNHCH_3]_3$.

It had been reported in an earlier report from this laboratory that decolorization of a potassium solution in liquid ammonia took place without H_2 evolution when a large excess of $[CH_3HNBH_2]_3$ was added to the ammonia solution. Attempts to verify the earlier observation have indicated that all decolorization is accompanied by H_2 evolution, and the previously described process has not been verified. Furthermore, the products from the $B_2H_6 \cdot 2NH_3$ -K reaction do not decolorize a solution of K in liquid ammonia without H_2 evolution.

2. Experimental

Run 1.—A sample of $(CH_3NHBH_2)_3$ (about 0.94 mM) was dissolved in about 3 ml of liquid NH_3 . The system was frozen down, and a sample of potassium metal, weighing 22.5 mg (equivalent to 0.565 mM) and sealed in a glass bulb by appropriate vacuum techniques, was added to the system and the bulb was broken. The system was warmed to $-78^\circ C$ and held at this temperature for 2 days. At the end of that time the blue color had disappeared and 0.860 mM of H_2 gas was measured. The H/K ratio is 3.04.

Run 2. The Reaction of Diammoniate of Diborane with Excess Potassium.— $B_2H_6 \cdot 2NH_3$ was prepared from 0.75 mM of B_2H_6 by conventional methods. To a liquid ammonia solution of the above reagent, 1.605 mM of K was introduced by conventional techniques [ratio $B_2H_6 \cdot 2NH_3/K = 1/2.14$]. The system was warmed to $-78^\circ C$. Although 0.368 mM H_2 was evolved (0.98 equiv. $H/B_2H_6 \cdot 2NH_3$), the blue color due to the measured excess of K remained. No direct evidence to support the existence of the compound $K_2[H_2BNH_2]$ has been obtained.

II. STUDIES OF THE AMINE-BORANES

A. FURTHER VAPOR-PRESSURE STUDIES OF THE AMINE-BORANES

Vapor-pressure measurements on the mono-, di-, and trimethylamine-boranes determined by the Knudsen effusion method have been reported previously.¹ However, since the heats of sublimation derived from the slope of the least-squares fit of the Clausius-Clapeyron equation appeared somewhat inconsistent, further measurements have been made to check the previous results and to extend the temperature range of the data. Experimental details have been given previously¹ and will not be repeated. Results were calculated from the relationship.²

$$P(\text{mm}) = 17.14 \frac{W}{K A t} \sqrt{\frac{T}{M}}$$

where W is the weight of the substance in grams effusing in time t in seconds through an orifice of area A square cm. M is the molecular mass and T is the absolute temperature. The constant, K , is a correction factor necessary to allow for the back reflection of molecules from the cylindrical walls of an orifice having a finite thickness. Values of this constant obtained by Clausius are tabulated by Dushman;³ in the present work, the two orifices used had K values of 0.935 and 0.865, respectively. Since the data previously reported had not been calculated using this factor, the corrected values of the earlier data together with those obtained more recently have all been included in the accompanying Table I. The data have also been fitted to the integrated form of the Clausius-Clapeyron equation by least-squares methods to give the vapor-pressure equations below. In the case of trimethylamine-borane, vapor-pressure data determined by conventional manometric techniques are available in the literature.⁴ Although these data are for higher temperatures and do not overlap the present results, the two sets of data appear consistent on a $\log P$ vs. $1/T$ plot. The equation for this compound consequently has been fitted to all data and covers the widest temperature range of the three substances.

Methylamine-borane:

$$\log_{10} P(\text{mm}) = - \frac{4114(1 \pm 0.053)}{T} + 11.411 (1 \pm 0.063)$$

range = 0° to 45°C

Dimethylamine-borane:

$$\log_{10} P(\text{mm}) = - \frac{4034(1 \pm 0.038)}{T} + 12.544 (1 \pm 0.042)$$

range = 0° to 35°C

Trimethylamine-borane:

$$\text{Log}_{10} P(\text{mm}) = - \frac{2962(1 \pm 0.014)}{T} + 9.894 (1 \pm 0.014)$$

range = 0° to 90°C

TABLE I

Methylamine-Borane		Dimethylamine-Borane		Trimethylamine-Borane	
Temp, °K	Pressure, mm	Temp, °K	Pressure, mm	Temp, °K	Pressure, mm
273.6	2.39×10^{-4}	273.8	7.78×10^{-3}	273.4	9.84×10^{-2}
292.8	1.63×10^{-3}	285.7	2.32×10^{-2}	274.2	1.04×10^{-1}
300.0	6.73×10^{-3}	285.7	2.52×10^{-2}	283.4	3.29×10^{-1}
300.0	6.60×10^{-3}	291.1	4.12×10^{-2}	283.4	3.27×10^{-1}
305.4	8.42×10^{-3}	294.0	5.90×10^{-2}	289.4	5.15×10^{-1}
306.9	1.03×10^{-2}	295.2	6.64×10^{-2}	289.4	5.16×10^{-1}
306.9	8.49×10^{-3}	299.2	1.11×10^{-1}	296.4	8.96×10^{-1}
309.1	1.41×10^{-2}	302.5	1.88×10^{-1}	297.5	8.19×10^{-1}
313.2	1.78×10^{-2}	306.0	2.49×10^{-1}	298.0	7.94×10^{-1}
314.4	1.96×10^{-2}	306.0	2.53×10^{-1}		

The uncertainties in the constants of the equations represent standard deviations calculated from the residuals between the points and the lines. Derived values for the heats of sublimation of the compounds are listed in Table II. The entropy of vaporization values are the standard entropy of vaporization at one atmosphere pressure and 25°C.

TABLE II

HEATS OF SUBLIMATION OF SOME AMINE-BORANES

Substance	$\Delta H_{\text{subl.}}$	ΔS_{298}°
$(\text{CH}_3)\text{NH}_2:\text{BH}_3$	$18.8 \pm 1.0 \text{ kcal}$	38.9 e.u.
$(\text{CH}_3)_2\text{NH}:\text{BH}_3$	18.5 ± 0.7	44.3
$(\text{CH}_3)_3\text{N}:\text{BH}_3$	13.6 ± 0.2	32.2

Inspection of the heat of sublimation values in Table II shows that the values for the mono- and dimethylamine compounds are approximately the same, while that for the trimethylamine complex is significantly lower. This suggests that a single hydrogen bond involving a hydrogen attached to nitrogen is important in the crystal structure of the first two compounds. Apparently the error in the earlier values of $\Delta H_{\text{subl.}}$, which differed significantly from the above results, can be attributed to the scatter of the points in conjunction with the rather short temperature range over which the measurements were made.

B. DIPOLE-MOMENT STUDIES OF THE AMINE-BORANES

1. Theoretical Studies

Because of the low vapor pressures of the amine-boranes, vapor-phase measurement of the dipole moments of these molecules appears to be impossible to effect with the equipment available here. Measurements in solution are always subject to the criticism that local solvent field effects may produce measured values which differ appreciably from the vapor-phase values which are of primary theoretical importance. One of the better approaches to this problem is the measurement of the dipole moment of each molecule in several solvents and a semi-empirical, semi-theoretical reduction of the data. A number of investigators have considered the theoretical problem represented by solvent-solute interaction. One can say that, to a zero-order approximation, all the resulting equations are the same, the square of the permanent dipole moment being related approximately linearly to the change in dielectric constant with solution concentration. The precise form of the relation varies from one equation to another depending on the assumption, stated or implied, as to the nature of the interaction between a particular dipolar molecule and the rest of the solution. In the conventional treatment, for example, one assumes that the molar polarization is the sum of various additive components. The physical picture corresponding to this assumption is cloudy, and its experimental weakness is shown by the fact that the dipole moment measured in solution differs from that measured in the vapor phase by an amount which may be roughly related to the dielectric constant of the solvent.

Several theoretical treatments of the problem, namely those of Onsager, Boettcher, and Scholte, have arisen from a set of clearly drawn physical assumptions regarding dipole-solvent interaction. It is well known that, although Onsager's equation gives reasonable values for the dipole moment of molecules measured in the pure liquid state, it does not show a similar improvement when applied to dilute solutions of polar molecules in nonpolar solvents. In fact, values for the dipole moment obtained from Onsager's equation usually deviate somewhat further from the vapor-state values than those obtained by the conventional method. It appears that Onsager's equation gives a fairly reliable picture of dipole-dipole interaction in pure liquids, but it offers little help in the interpretation of the interaction between dipoles and nonpolar solvent molecules.

Boettcher modified Onsager's treatment by introducing the assumption that the volume of the molecule should be regarded as smaller than its partial molar volume in the liquid or, in other words, that there is free space in the liquid. Such an assumption simply introduces two additional parameters into the equation and should result in a better fit of the experimental data regardless of the validity of the postulates made.

The equation of Scholte introduces two further parameters. In addition to the average molecular radius and average polarizability of the molecule involved in Boettcher's equation, it recognizes the anisotropy of the molecule and includes constants for length and polarizability along the axis of the dipole.

In order to evaluate the treatments of Boettcher and Scholte, the data of Pilpel on solutions of acetophenone and benzonitrile in benzene were used. After a rather exhaustive evaluation, it was concluded that the analysis of Boettcher was not particularly appropriate to the immediate data and ultimate problem under consideration. A method of plotting was devised by which Scholte's equation could be tested using the dielectric constant data in the dilute solution region. If data were restricted to solutions containing less than 10 mole percent solute, a modified form of Scholte's equation fit the data well and gave the correct value for the dipole moment of the solute molecule. For concentrations above 10 mole percent, both the acetophenone and benzonitrile showed rather sudden and large deviations. The validity of the modified Scholte equation in reducing data on the amine-boranes is to be investigated further and will be reported in a subsequent paper.

2. Experimental Measurements

(a) Preparation of Methylamine-Borane.—In the course of these investigations, methylamine-borane was prepared for the first time as a stable solid which melted sharply at 54°C . Although mentioned in an earlier report, the preparative procedure has not been previously described; hence it is included herein.

Diborane was distilled twice at the temperature of methylcyclohexane slush to remove higher hydrides. About 50 millimoles of B_2H_6 were added slowly at -78°C to 15 ml of liquid tetrahydrofuran [previously dried over LiAlH_4]. Commercial anhydrous methylamine (Matheson) was dried over sodium and about 2 ml of the liquid were distilled into the reaction tube containing the tetrahydrofuran solution of B_2H_6 . A slush bath at -112°C was placed around the reaction tube and the system was allowed to stand. The temperature rose gradually. The solvent and excess amine were removed when the temperature reached 45°C ; the system was then allowed to warm to room temperature for a few minutes to aid in solvent removal. Finally the reaction tube was surrounded with ice and the last traces of amine and solvent were removed by pumping on the system with the high-vacuum pump for 10 hours. Trimethylamine-borane and dimethylamine-borane should sublime under these conditions.

A cold finger was then inserted into the reaction tube, the sample was warmed to room temperature, and MeNH_2BH_3 was sublimed onto the cold finger as large rectangular crystals. After about half of the product had sublimed, the residue liquified. The sublimation was then discontinued and the residue discarded.

The pure product melts sharply at 54°C . It is soluble in ethyl ether and dioxane, and dissolves with difficulty in benzene. Analysis of the sample showed: hydridic H = 6.64%, B = 23.8%; calculated values for $\text{CH}_3\text{NH}_2\text{BH}_3$ are: hydridic H = 6.68%, B = 24.10%.

(b) Calibration of Equipment.—In all previous dipole measurements, only a small portion of the total range of the measuring condenser was used; hence deviations from linearity were unimportant. However, in the extended measurements now in progress, a wider range of the condenser scale is involved and calibration was desirable. The condenser scale has been calibrated using conventional methods. The precision refractometer was also calibrated using the glass reference piece supplied with the instrument.

(c) Dipole-Moment Measurements.—The moments of mono-, di-, and trimethylamine-boranes have been measured in benzene, ethyl ether, and dioxane. Mono-methylamine was prepared as described above and transfers were made in the dry box. Dimethylamine-borane from Callery Chemical Company was sublimed several times and sublimed into the weighing cell before use. Trimethylamine-borane, prepared from prepurified B_2H_6 and Me_3N , was sublimed into the reaction vessel.

The three solvents, reagent grade benzene, "anhydrous" ether, and dioxane, were refluxed with LiAlH_4 for from 6 to 12 hours, then put on the vacuum line and distilled through a frit into a glass storage vessel. Solvent was transferred to the weighing cells by means of a hypodermic syringe.

Data from the runs have not been completely analyzed, but significant differences between measurements in different solvents have been observed and are being considered in relation to the theoretical problem outlined in the earlier section.

C. RAMAN SPECTRAL STUDIES OF THE AMINE-BORANES

Reference has been made in previous reports to the conclusion, based on work with the amine-boranes, that the frequency assigned to the boron-nitrogen dative bond in the literature is too high. The evidence supporting this conclusion is summarized as follows.⁵

The bond in question is one of the more stable of the dative bonds to boron and in complexes of boron trifluoride with ammonia⁶ and nitrogen heterocycles,⁷ frequencies lying in the range between 980 and 1120 cm^{-1} have been assigned. In the complex of boron trimethyl with ammonia, a value of 1105 cm^{-1} has been chosen⁸

and in the complex of borane (BH_3) with nitrogen trimethyl, $[\text{N}(\text{CH}_3)_3]$, a value of 1250 cm^{-1} has been proposed.⁹ By way of comparison, frequencies assigned to the covalent carbon-carbon bond in halogenated ethane derivatives, where the masses involved are comparable, fall in the range between 800 and 1000 cm^{-1} with very few exceptions. It is, of course, not always a proper comparison merely to look at the magnitude of frequencies in complete disregard of other factors. Nevertheless, chemical data seem to indicate a lower range for this stretching frequency of the boron-nitrogen dative bond.

In the case of ammonia-borane, it has been possible to identify the B-N frequency unambiguously as a well-polarized band of medium intensity at 785 cm^{-1} in liquid ammonia solution. The assignment can be made with a high degree of confidence for this compound in contrast to those reported in the literature because of the relative simplicity of the spectrum below 1200 cm^{-1} . Confirmation of the assignment is amply supplied by the results obtained from the several isotopic derivatives studied. To a first approximation, the NH_3 and BH_3 groups may be considered rigid and treated as point masses. The boron-nitrogen frequency of the isotopic species should then be calculable from the reduced masses of the pseudo-diatomic molecules. In Table III the observed frequency ratios have been compared with the appropriate mass ratios and it is seen that the agreement is excellent, the largest deviation being about 2%. The simple boron-nitrogen stretching force constant calculated from the hydrogen compound datum to this approximation is $2.8 \times 10^5 \text{ dynes/cm}$.

TABLE III

COMPARISON OF THE BORON-NITROGEN STRETCHING FREQUENCY IN ISOTOPIC DERIVATIVES OF AMMONIA-BORANE IN LIQUID AMMONIA SOLUTION

Compound	$\nu(\text{B-N}),$ cm^{-1}	ν^*/ν	$\sqrt{\mu/\mu^*}$
$\text{H}_3\text{N}:\text{BH}_3$	785	--	--
$\text{H}_3\text{N}:\text{BD}_3$	737	0.94	0.95
$\text{D}_3\text{N}:\text{BH}_3$	754	0.96	0.97
$\text{D}_3\text{N}:\text{BD}_3$	708	0.90	0.91
$\text{D}_3\text{N}:\text{B}^{10}\text{D}_3$	713	0.91	0.93

In the case of the methylamine derivatives, the band in question appeared with approximately the same intensity and depolarization characteristics but with decreasing frequency as the number groups on the nitrogen increased (Table IV).

Examination of the spectrum of the trimethylamine complex prepared with boron-10 in 96% enrichment showed that the assigned band at 667 cm^{-1} in the normal compound shifted to 676 cm^{-1} in the isotopic. The band near 1250 cm^{-1} as-

TABLE IV

THE BORON-NITROGEN STRETCHING FREQUENCY OF THE
METHYLAMINE-BORANES (DIMETHYL ETHER SOLUTION)

<u>Amine</u>	<u>Frequency, cm⁻¹</u>
Ammonia	755
Methylamine	726
Dimethylamine	696
Trimethylamine	667

signed to the B-N frequency by Rice *et al.*,⁹ however, was found to shift only 2 cm⁻¹, which is approximately the precision of the measurements. The literature assignment thus appears doubtful, particularly since the 1250-cm⁻¹ band is weak in the Raman effect.

The spectral range within which the boron-nitrogen frequency is assigned in the present investigation is in good agreement with the frequencies available for other dative bonds to boron in complexes of borane with ligands such as carbon monoxide, phosphorus trifluoride, and dimethyl ether.

The boron-hydrogen stretching region in the spectra of the amine-boranes studied is markedly similar. In each case there are two strong bands appearing at approximately 2270 and 2370 cm⁻¹ plus a weaker, rather diffuse band at about 2330 cm⁻¹. The actual figures are listed in Table V.

TABLE V

FREQUENCIES IN THE HYDROGEN STRETCHING REGION IN THE
RAMAN SPECTRA OF THE METHYLAMINE-BORANES

H ₃ NBH ₃	MeH ₂ NBH ₃	Me ₂ HNBH ₃	Me ₃ NBH ₃	Me ₃ NBH ₃ (Ref. 9)
2273 s,p	2266 s,p	2260 s,p	2268 s,p	2266 (10), p
2326 w,d	2328 w	2332 w	2330 w	2330 (3) dif.
2373 s,p	2367 s	2368 s	2369 s,p	2372 (10), d

Symbols: s = strong, w = weak, dif. = diffuse, p = polarized, d = depolarized

In ammonia-borane, the polarization measurements have shown clearly that two intense bands are both strongly polarized while the intermediate band appears to be depolarized. Accordingly, the 2273-cm⁻¹ band has been assigned as the symmetric B-H stretching mode, the 2326-cm⁻¹ band as the asymmetric mode, and the 2373-cm⁻¹ band as the overtone of the intense band at 1175 cm⁻¹ in Fermi reso-

nance with the symmetric B-H mode.

In the amine-boranes, the polarization characteristics of these bands have been more difficult to determine since the degree of polarization is less. Rice and his co-workers,⁹ in their work on trimethylamine-borane, report the 2372-cm^{-1} band to be depolarized and assign the 2266- and 2372-cm^{-1} bands to the symmetric and asymmetric B-H bands, respectively, leaving the intermediate band at 2330 cm^{-1} for the overtone. This assignment does not fit with the ammonia-borane data.

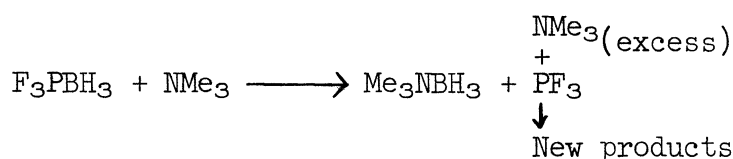
The polarization properties of the trimethylamine-borane Raman bands in liquid ammonia solution have now been examined more carefully and the results indicate that the highest band at 2372 is indeed polarized and should therefore be assigned to a totally symmetric vibration, namely to the overtone. This assignment is not entirely unequivocal because of the large uncertainty associated with the measurements but it is in agreement with the ammonia borane results.

Experimental difficulties have prevented carrying out the projected work on the infrared spectrum of these compounds at low temperatures.

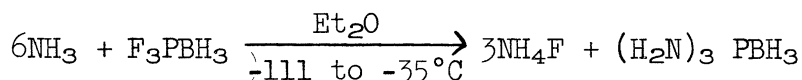
III. THE REACTION OF PHOSPHORUS TRIFLUORIDE-BORANE AND AMMONIA

A. BACKGROUND

In the original studies on the preparation of H_3BPF_3 ,¹⁰ it was found that trimethylamine replaced the weak base PF_3 if H_3BPF_3 and NMe_3 were mixed in a one-to-one mole ratio. Addition of excess trimethylamine then resulted in an unspecified reaction between PF_3 and NMe_3 . The process can be represented as:

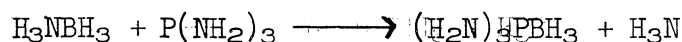
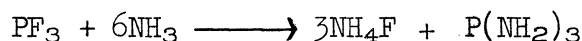
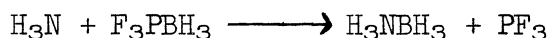


As noted in the last report from this laboratory, ammonia reacts with F_3PBH_3 in a different manner. The reaction is represented by the equation:



The new ether soluble product, triamido-phosphorus borane was characterized by analysis and molecular weight values.

In a formalistic sense the reaction of H_3N and F_3PBH_3 was compared to the reaction of H_3N and F_3PO and it was of some academic interest to decide whether the reaction was a direct one involving attack of H_3N on F_3PBH_3 , or whether the reaction proceeded in a more conventional fashion by the process:



The first equation in the above sequence would be directly analogous to the reaction between trimethylamine and F_3PBH_3 . A direct test of the above postulate could be made by mixing H_3NBH_3 , PF_3 , and NH_3 . If reaction proceeded as described above, $(H_2N)_3PBH_3$ and NH_4F should appear as products. Experimentally it was found that no $(H_2N)_3PBH_3$ could be detected in the products and some of the original H_3NBH_3 remained unchanged. These data support the hypothesis that the reaction proceeds through direct attack of NH_3 on F_3PBH_3 without initial rupture of the P-B bond. In this sense the analogy with F_3PO is supported.

B. EXPERIMENTAL

1. The Reaction Between H_3NBH_3 , PF_3 , and NH_3

Ammonia-borane (0.363 millimole) was dissolved in about 2 ml of diethyl ether. An approximately equimolar quantity of PF_3 (0.368 mM) was condensed into the reactor and the system was allowed to warm up to -78°C . No external signs of reaction appeared. The solution remained clear and transparent and no gas evolution was detected. The system was frozen with liquid nitrogen and a large excess of ammonia (4.31 mM) was condensed into the reactor. The temperature was then allowed to rise slowly to -78°C and this temperature was maintained for 10 hours. Finally the temperature was raised to -35°C and kept at this temperature for several hours. The reaction mixture was filtered through the vacuum line filtration apparatus and the volatile components were removed from the filtrate and fractionated. The recovered ammonia amounted to 3.07 mM; thus 1.24 mM appeared to have been used in the reaction. The ratio of NH_3 consumed to PF_3 used is $1.24/0.368$ or 3.37. The value is below the ratio of the 6 to 1 predicted by the equation for the complete ammonolysis of PF_3 . (See second equation in above sequence.) The solid product remaining after removal of the volatile components from the filtrate was examined by X-ray powder methods. NH_3BH_3 was detected in the solid but no lines for $(\text{NH}_2)_3\text{PBH}_3$ were found.

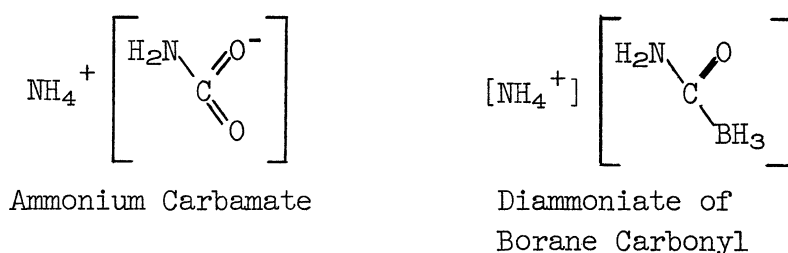
2. X-ray Crystallographic Data on $(\text{NH}_2)_3\text{PBH}_3$

A structural study using single-crystal X-ray methods is in progress on this compound. Single crystals have been prepared, mounted, and photographed. The crystals are monoclinic with the approximate cell parameters: $a = 9.38\text{\AA}$, $b = 9.47\text{\AA}$, $c = 6.21\text{\AA}$, $\beta = 100.2^\circ$. The unit cell contains four molecules. The space group $\text{P}2_1/\text{C}$ is unambiguous. Three-dimensional data have been collected and visually evaluated. The locations of the four phosphorus atoms in the unit cell have been found from hko and okl Patterson projections. The determination of the complete structure is in progress.

IV. THE CHEMISTRY AND STRUCTURE OF THE DIAMMONIATE OF BORANE CARBONYL

A. BACKGROUND

One of the few relatively simple boron hydride addition compounds whose structure remains mysterious is $H_3BCO \cdot 2NH_3$ or the diammoniate of borane-carbonyl. Reasoning from analogy, members of this laboratory suggested a structure analogous to ammonium carbamate:



Experiments designed to further the chemistry of the diammoniate of borane carbonyl and to test the above structural proposal are in progress.

B. EXPERIMENTAL

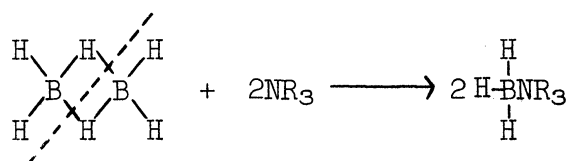
$H_3BCO \cdot 2NH_3$ was prepared by adding an excess of ammonia to 2.98 mM of H_3BCO , warming to $-126^\circ C$ for 30 minutes, warming to $-78^\circ C$, and allowing the system to stand at this temperature for 18 hours. The ammonia was then removed at $-78^\circ C$ and finally at $0^\circ C$ until the white solid remaining evolved no more NH_3 . This solid gave off a noncondensable gas, presumably H_2 , fairly rapidly at room temperature (approximately 0.1 mM/hr). The ammonia was then returned to the reactor and a liquid of low vapor pressure remained in the U-trap where the ammonia had been stored. The nonvolatile liquid was allowed to remain in contact with excess ammonia at $-78^\circ C$ for three days. At the end of this time the ammonia was removed again from the U-trap and a white solid remained. It is assumed that the solid is $H_3BCO \cdot 2NH_3$ and that the liquid of low vapor pressure represents a reaction intermediate.

To the sample of solid NH_3 and $H_3BCO \cdot 2NH_3$ in the original reactor at $-196^\circ C$ a large excess of sodium was added. As the temperature rose slowly, the solid ammonia melted and sodium went into solution. From this system 1.07 mM of hydrogen were evolved quite rapidly. On warming to $-45^\circ C$ for 40 hours 1.04 mM of additional hydrogen were evolved. Since some of the original H_3BCO was removed with the ammonia into the U-trap, a precise analysis of the stoichiometry of the sodium reaction cannot be made from the data available, but the qualitative observations are in agreement with the observations of Burg and Schlesinger.⁴ The system is being explored further. Additional simple and exploratory chemical studies appear mandatory.

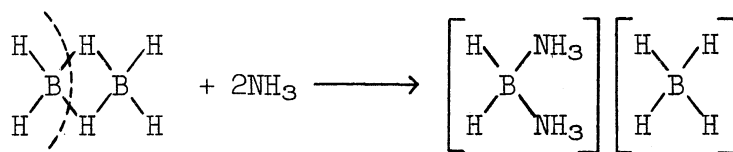
V. TETRABORANE—THE CHEMISTRY OF ITS REACTIONS
WITH VARIOUS BASES AND THE STRUCTURE OF THE PRODUCTS FORMED

A. BACKGROUND

The chemistry of diborane, as interpreted in this laboratory, usually involves the bridge bonds as centers of reactivity. So-called symmetrical and non-symmetrical cleavage processes have been recognized on the basis of the products obtained. Thus diborane will undergo two reactions as indicated below:

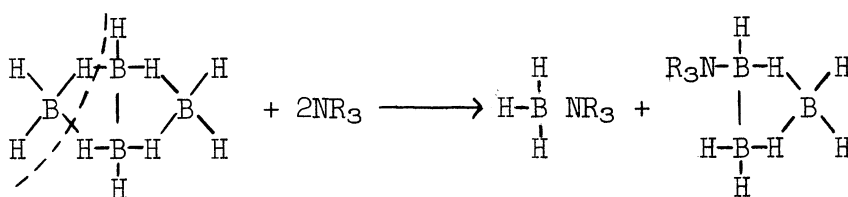


Symmetrical Cleavage

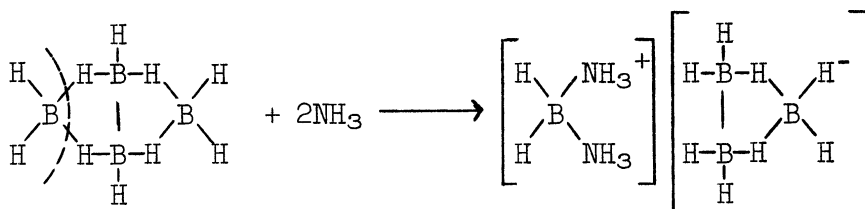


Nonsymmetrical Cleavage

Tetraborane likewise has a double bridge bond and the same type of cleavage patterns has been recognized. (See earlier reports from this laboratory.)

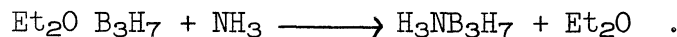


Symmetrical Cleavage



Nonsymmetrical Cleavage

Only chemical evidence was used in establishing the nonsymmetrical cleavage of the double bridge bond in tetraborane by ammonia. The symmetrical ammonia cleavage product could be made by indirect methods, e.g.:

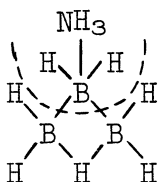


Its structure has been worked out by X-ray methods and earlier reports have given an account of this work as it progressed.

B. THE STRUCTURE OF AMMONIA-TRIBORANE, $\text{H}_3\text{NB}_3\text{H}_7$ (LOW-TEMPERATURE FORM)

The refinement of this structure by least-squares methods has been further improved by the use of individual isotropic thermal parameters for all atoms, except the hydrogens of the NH_3 group. The final refinement yielded a value of 0.107 for the residuals.

The structure of the B_3H_7 group resembles a fragment of the B_4H_{10} molecule and is in agreement with the symmetrical cleavage hypothesis outlined above; however, rather significant (and not unexpected) distortions of the parent tetraborane structure are observed due to replacement of BH_3 by NH_3 . As a result of these distortions, an alternative structural interpretation can be suggested, namely, that $\text{B}_3\text{H}_7 \cdot \text{NH}_3$ can be considered as a bridge substituted diborane:



The above model suggests the interesting possibility of synthesizing $\text{R}_3\text{NB}_3\text{H}_7$ from the reaction: $\text{R}_3\text{NBH}_3 + \text{B}_2\text{H}_6 \longrightarrow \text{R}_3\text{NB}_3\text{H}_7 + \text{H}_2$. Such a possibility is under examination. A paper on the structure of $\text{H}_3\text{NB}_3\text{H}_7$ has been completed and will be submitted for publication.

C. PHYSICAL PROPERTIES OF $\text{H}_3\text{NB}_3\text{H}_7$ AND $\text{Me}_3\text{NB}_3\text{H}_7$

1. Infrared Spectra of $\text{H}_3\text{NB}_3\text{H}_7$ and $\text{Me}_3\text{NB}_3\text{H}_7$

Preliminary infrared spectra of $\text{H}_3\text{NB}_3\text{H}_7$ and $\text{Me}_3\text{NB}_3\text{H}_7$ have been obtained. Due to the low solubility of these compounds in the customary solvents, the spectra have not been entirely satisfactory for detailed analysis. The results available indicate that, in the ammonia complex the bridge-stretching frequencies have been shifted from their abnormally high value in tetraborane down into their customary region between 1500 to 2000 cm^{-1} . However, in the spectra of the trimethylamine complex, a much smaller effect on these bands is apparent and their position is still unusually high. It is tempting to postulate that this evidence implies a stronger interaction between ammonia and triborane than between trimethylamine and triborane, a conclusion which is in agreement with prejudices arising from coordination theory.¹¹ It is obvious that a more detailed and careful analysis must be made for reliable conclusions.

2. Vapor Pressure of $\text{H}_3\text{NB}_3\text{H}_7$

Vapor-pressure data reported previously for ammonia-triborane were not corrected for the orifice thickness (cf. Section II-A of this report). The revised values are tabulated below together with the vapor-pressure equation obtained by a least-squares fit of the integrated Clausius-Clapeyron equation.

<u>Temperature, °K</u>	<u>Pressure, mm</u>
303.6	7.76×10^{-4}
309.6	1.31×10^{-3}
314.2	1.99×10^{-3}
319.4	3.15×10^{-3}
327.0	5.81×10^{-3}

$$\text{Log}_{10} P(\text{mm}) = - \frac{3739 (1 \pm 0.0075)}{T} + 9.200 (1 \pm 0.0096)$$

(range: 30 to 55°C)

The derived heat of sublimation is $\Delta H_{\text{subl.}} = 17.11 \pm 0.13$ kcal/mole and the standard entropy of vaporization at 25°C and one atm. is $\Delta S^\circ = 28.9$ e.u. It is of interest to note that the heat of sublimation is approximately equal to that of the amine-boranes having at least one hydrogen on the nitrogen atom.

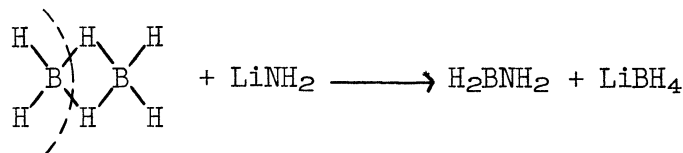
D. THE STRUCTURE OF $\text{B}_4\text{H}_{10} \cdot 2\text{NH}_3$ BY X-RAY CRYSTALLOGRAPHY

The currently accepted model for $\text{B}_4\text{H}_{10} \cdot 2\text{NH}_3$ is based entirely on chemical evidence. Although such evidence is considered to be very strong, independent physical evidence on the structure is desirable. A single crystal of $\text{B}_4\text{H}_{10} \cdot 2\text{NH}_3$ has been prepared, mounted, and photographed for single-crystal X-ray studies. The compound is orthorhombic with the approximate cell parameters $a = 9.26\text{\AA}$, $b = 9.42\text{\AA}$, $c = 8.22\text{\AA}$. The unit cell contains four molecules giving a calculated density of 0.809 g/cm³. The space group is either C_{2v}^9 -Pbn2, or D_{2h}^{16} -Pbnm. Complete three-dimensional data have been recorded using an integrating Weissenberg camera. The more than 400 observed reflections are now being measured using a photoelectric densitometer.

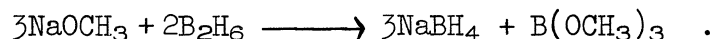
E. THE REACTIONS OF B_4H_{10} WITH KBH_4 , KOH , AND KOCH_3 — THE PREPARATION OF KB_3H_8

1. Background

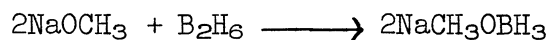
Up to the present time, NH_3 is the only reagent which is known to give non-symmetrical cleavage of the double bridge bonds in tetraborane. In diborane, G. Schaeffer and his co-workers¹² have obtained evidence for the reaction of LiNH_2 with B_2H_6 to give LiBH_4 and H_2BNH_2 , a process which can be interpreted in terms of a nonsymmetrical cleavage of the bridge bonds of B_2H_6 .



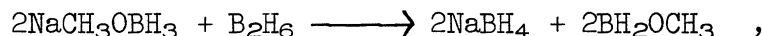
Similarly, Schlesinger, Brown, and their collaborators¹³ reported that B_2H_6 reacts with NaOCH_3 in accordance with the equation:



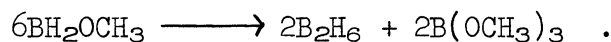
In the original paper the reaction was interpreted in terms of a symmetrical cleavage:



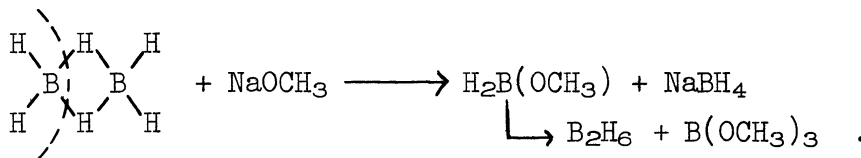
followed by further reaction with diborane:



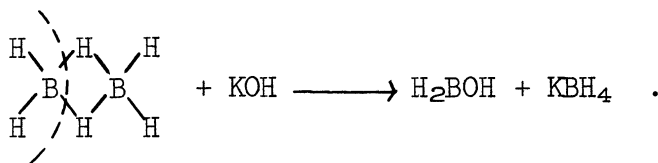
and a disproportionation:



It is of interest to note, however, that one can interpret the products obtained as evidence for a nonsymmetrical cleavage process comparable to that observed for LiNH_2 .

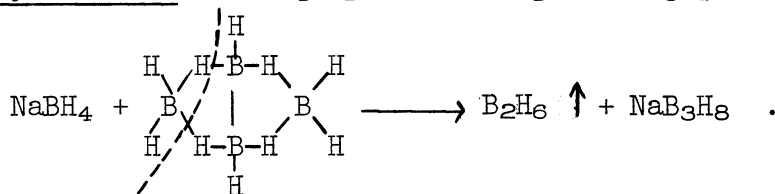


Similarly, a report by Winternitz¹⁴ indicated that the reaction of B_2H_6 with a cold concentrated solution of KOH gave significant yields of KBH_4 , a fact which can also be interpreted in terms of a nonsymmetrical cleavage process.

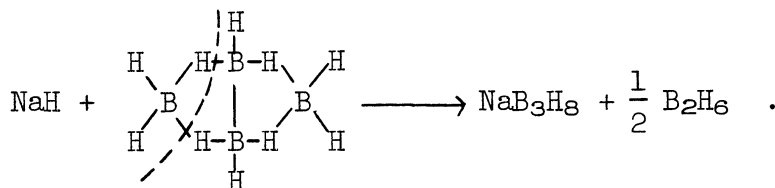


All the foregoing interpretations relative to the nonsymmetrical cleavage of diborane are equivocal in that one cannot rule out a symmetrical cleavage followed by a subsequent reaction which gives the observed products. On the other hand, the cleavage pattern of tetraborane is subject to more certain interpretation since "symmetrical cleavage" gives H_3B and B_3H_7 fragments rather than two H_3B fragments as in diborane. Accordingly, the reaction of tetraborane with KOCH_3 , KOH , and KBH_4 has been studied to determine the cleavage pattern expected with these reagents.

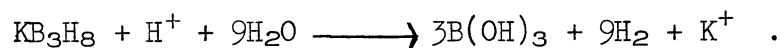
Potassium hydroxide, potassium methoxide, and potassium borohydride were each allowed to react with tetraborane in diethyl ether slurry at 0°C. Edwards and his collaborators at Callery Chemical Company have established that NaBH₄ reacts with tetraborane by a symmetrical cleavage process to give NaB₃H₈. The equation is:



It was reported by Edwards and Hough¹⁵ that sodium hydride reacts in a similar fashion:

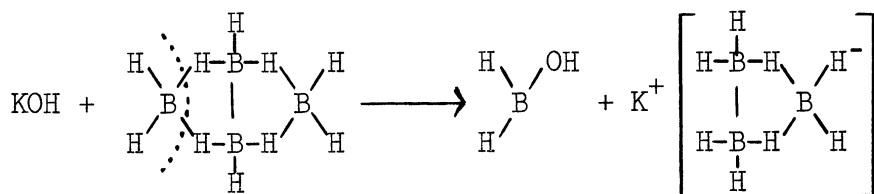


The KBH₄-B₄H₁₀ reaction was employed in this study as a means of preparing an authentic sample of KB₃H₈. The reaction gave a solid product with a hydrogen-boron ratio of 3 to 1 as determined by acid hydrolysis. The theoretical hydrolysis equation would be:

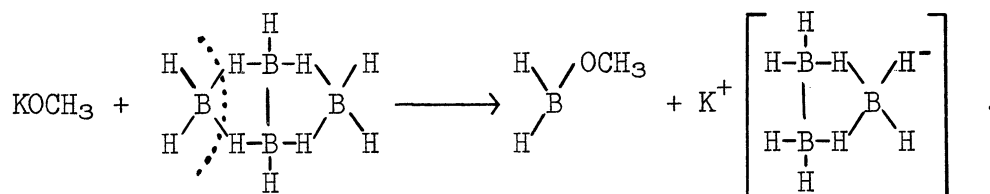


Thus the ratio expected for KB₃H₈ would be H₂/B = 3/1 as observed. Complete analytical data are not yet available, and the absolute analytical values for B and H are about 20% low for KB₃H₈ suggesting the possibility of solvent in the sample. The product is slightly soluble in ethyl ether, but very soluble in tetrahydrofuran. The solid gives a definite and characteristic X-ray powder pattern. Although characterization is as yet incomplete, the evidence supporting the formula [KB₃H₈ + some solvent] is good.

On the basis of still incomplete evidence, the reactions of KOH and KOCH₃ with tetraborane can be represented by the nonsymmetrical cleavage equations:



and



The processes are always accompanied by side or subsequent reactions. Appreciable quantities of H_2 gas were evolved, probably as a result of reactions involving H_2BOH and H_2BOCH_3 . Neither H_2BOH nor H_2BOCH_3 were isolated from the process. The latter compound has been described as a solid which decomposes slowly to B_2H_6 and $B(OCH_3)_3$. The solid identified as KB_3H_8 gave a powder pattern which was identical to the solid tentatively identified as KB_3H_8 resulting from the $KBH_4-B_4H_{10}$ reaction.

2. Experimental

(a) $KBH_4-B_4H_{10}$.—Commercial KBH_4 (Metal Hydrides) was allowed to react at $0^\circ C$ for 3 hours with a slight excess of B_4H_{10} in diethyl ether. The KBH_4 was slurried in the ether; it is not soluble. The system was filtered in the vacuum line filtration system and the diethyl ether filtrate was separated. It left virtually no solid when the ether was distilled out. The solid on the filtering disc was then leached with tetrahydrofuran. From this filtrate a white solid, presumably KB_3H_8 , was crystallized out as the THF was removed. Its characterization is as yet incomplete.

(b) Reaction $KOH-B_4H_{10}$.—Several pellets of commercial reagent grade KOH were placed in a reaction tube; the tube was fastened to the vacuum system, evacuated, and about 5 ml of diethyl ether were condensed into the system. A sample of B_4H_{10} (5 mM) was condensed into the system and it was stirred constantly as the temperature gradually rose to $0^\circ C$. The solid phase was separated by filtration; then it was leached with tetrahydrofuran. Removal of the THF by distillation left a solid, the X-ray powder pattern of which is identical to that of the product, presumably KB_3H_8 , of part (a).

(c) Reaction $KOCH_3-B_4H_{10}$.—Potassium metal sealed in a bulb by standard techniques (3.57 mM) was broken into a reaction tube under a stream of dry nitrogen; then the tube was attached to the vacuum line. A sample of CH_3OH (slightly more than 3.57 mM) was condensed into the tube and allow to react with the potassium by raising the temperature slowly. The H_2 evolved and the excess of CH_3OH was pumped from the system; about 5 ml of ethyl ether and 5.42 mM of B_4H_{10} were condensed in the tube and the system was allowed to warm to $-78^\circ C$ and maintained at this temperature for 30 minutes. The $KOCH_3$ slowly dissolved to give a clear solution; then a white precipitate began to form. The system was then allowed to warm up to $-35^\circ C$; it was held at this temperature for 30 minutes; then filtered in the vacuum line filtration assembly. As the filtrate was warmed to room temperature a white precipitate formed, indicating incomplete reaction prior to filtration. The solid product was leached from the filter with tetrahydrofuran. When the solvent was removed, the solid gave an X-ray powder pattern which is identical to that of the earlier product identified tentatively as KB_3H_8 .

F. THE RAMAN AND INFRARED SPECTRA OF TETRABORANE

A study of the vibrational spectrum of tetraborane has been started. The infrared spectrum of this substance has been published but no interpretation has been given.¹⁶ The Raman spectrum has not been obtained. The spectrum of this boron hydride is unique since the stretching frequencies associated with the bridge hydrogen atoms do not occur in the region in which they are found in the other boron hydrides. The conventional bridge frequencies are found in the region 1500-2000 cm^{-1} , yet this region is clear in the spectrum of B_4H_{10} . The frequencies tentatively attributed to the bridge hydrogens in the preliminary spectrum appear in the region around 2150 cm^{-1} .

The preliminary spectra gave evidence of B-2 and B-5 impurities in the tetraborane and considerable time was devoted to obtaining spectroscopically pure material.

VI. STUDIES ON BRIDGE COMPOUNDS RELATED TO BORON HYDRIDES

A. FURTHER STUDIES ON $F_3PAI_3Cl_3$, OBTAINED FROM Al_2Cl_6 AND PF_3 . THE FLUORIDE SHIFT IN THE PF_3 ADDUCTS

1. Background

The compound Cl_3AlPF_3 , formerly assumed to be too unstable for isolation, was prepared in this laboratory and has been described in earlier reports. A characteristic reaction of this compound is an internal shift of F^- and Cl^- to give AlF_3 and PCl_3 as ultimate products. This process looked particularly interesting since it represents another example of an internal shift of ligands in these Lewis acid-base complexes. The process can be formalistically compared to the shift of OCH_3^- and H^- groups found in the previously described compound $H_3BN(CH_3)_2OCH_3$, etc.¹⁷

It has been assumed that $F_3PAI_3Cl_3$ is formed initially by interaction of the lone pair electrons of PF_3 with the aluminum of $AlCl_3$. It is then assumed that a fluorine of PF_3 is transferred to the Al of $AlCl_3$ (temporary coordination number of 5 for Al) and that this is followed by a shift of Cl^- to the P. It appears that it should be possible to isolate intermediates of the form PF_2Cl , $PFCl_2$, etc., by careful control of the conditions of the rearrangement. Such a study has been conducted and is described in the following subsection.

2. Experimental. The System $PF_3-Al_2Cl_6$

Attempts to isolate mixed phosphorus halides from the decomposition of $F_3PAI_3Cl_3$ have been unsuccessful.

A sample consisting of 19.95 mM PF_3 was condensed onto 0.58 mM of Al_2Cl_6 . After standing at room temperature under 8 atm pressure for three hours, there was no evidence of a liquid phase and thus of PCl_3 formation, but the complex Cl_3AlPF_3 had formed. From the reaction vessel 18.84 mM of PF_3 was recovered, leaving 1.11 mM of PF_3 consumed in the reaction or a ratio of 0.96 mole PF_3 per formula weight $AlCl_3$. The complex was never warmed above $-112^\circ C$ after removal of excess PF_3 except as specifically noted below. About 35 mM PF_3 was condensed on the sample and left at $-112^\circ C$ for three hours. During this period a cloudiness (presumably AlF_3) began to develop in the PF_3 solvent. Another 30 mM PF_3 were added and after two more hours at $-112^\circ C$ there was a large amount of precipitate. PF_3 was removed at $-150^\circ C$ and the molecular weight of the last portion of vapor to come off was measured. A value of 86 (theoretical for $PF_3 = 88$) indicated the absence of PF_2Cl or $PFCl_2$ in that fraction. No volatile fraction was obtained at $-112^\circ C$; however, at $-63^\circ C$ a volatile fraction identified as

0.75 mM PCl_3 was separated. (V.P. PCl_3 = 40 mm at 0°C , PFCl_2 = 450 mm at 0° ; sample = 41 mm at 0°C .) The tube was then warmed to 0°C and an additional 0.34 mM of PCl_3 was recovered representing about 98% of the original phosphorus consumed in compound formation.

The fact that no mixed halides were ever isolated indicates that halide shift occurs more easily than dissociation of the complex.

The foregoing observations indicate that in excess liquid PF_3 , the halogen shift occurs even at -112°C , but the reaction is sufficiently slow so that the molecular weight of the complex as determined in liquid PF_3 is valid if only fresh solutions are considered. (See earlier reports.)

The reaction time for preparation of the complex seems to be about 3 hours if very pure PF_3 is used; however, PF_3 with traces of HCl (colorless solution red in liquid state) seems to slow down halogen exchange in the complex and the system may be held for 4 hours at room temperature without appreciable exchange occurring.

3. The Decomposition of $\text{Pt}(\text{PF}_3)_2\text{Cl}_2$

Earlier observations in this laboratory had suggested that the product obtained from the thermal decomposition of $\text{Pt}(\text{PF}_3)_2\text{Cl}_2$ might be an authentic mixed halide PF_2Cl or PFCl_2 . Preliminary observations on this system have been inconclusive due to the presence of NH_4Cl in the reaction system.

B. THE REACTION OF PF_3 AND Al_2Me_6

Preliminary studies on the system PF_3 - Al_2Me_6 have been carried out. Experimental techniques have been developed using grease-free systems. The reaction is more difficult experimentally than the PF_3 - Al_2Cl_6 reaction. It is rather clearly established that a reaction occurs between PF_3 and Al_2Me_6 but the stoichiometry has been poor and nonreproducible; products have not yet been identified. Some evidence for the formation of PMe_3 has been obtained.

C. THE ALUMINUM HYDRIDE-BIS TRIMETHYLAMINE COMPLEX

1. Dipole-Moment Measurements

The dipole moment of the compound $\text{H}_3\text{Al}(\text{NMe}_3)_2$ has been determined in benzene solution using the standard heterodyne beat apparatus described in earlier reports. A value of 1.3 Debyes has been obtained for the compound in benzene solution.

2. Single-Crystal X-Ray Studies

A single crystal of the compound has been prepared, mounted, and photographed.

The data are now being reduced.

Preliminary information as noted below is now available.

- (a) Lattice type is orthorhombic; $a = 8.85\text{\AA}$, $b = 10.10\text{\AA}$,
 $c = 12.93\text{\AA}$.
- (b) Number of molecules/unit cell = 4.
- (c) Space group $Ccmb$ or $Cc2a$.

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