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THE CHEMISTRY OF BORON HYDRIDES

AND RELATED HYDRIDES

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R. W. Parry
Goji Kodama
S. G. Shore
R. C. Taylor
Earl Alton

OBJECTIVE

A continuation of fundamental studies on the chemistry of the hydrides of boron and related compounds.

ABSTRACT

The ammonolysis of H_2BNH_2 has been studied and an explanation of pertinent facts has been suggested.

Additional data on the system $B_4H_{10}-NH_3$ indicate that the highest ammoniate may be $B_4H_{10}-6NH_3$. The study is being continued.

Force constants for the borohydride ion and for the borane carbonyl molecule have been calculated from the Raman spectrum and are reported.

Molecular-weight data on the system $B_2H_6 \cdot 2NH_3$, prepared at $-45°C$, have been rechecked and earlier results are confirmed.

The compound Cl_3AlPF_3 has been prepared and its properties are briefly described.

I. THE REACTIONS AND STRUCTURE OF THE
DIAMMONIATE OF DIBORANE

A. MOLECULAR-WEIGHT MEASUREMENTS IN LIQUID AMMONIA FOR SAMPLES OF THE
DIAMMONIATE PREPARED AT -45°C

In an earlier report[1] it was noted that the molecular weight of the diammoniate prepared at -45° differs from that of the "diammoniate" prepared at -78°C. The desirability of additional confirmatory evidence was indicated. Some of the needed data have been obtained. Earlier results have been confirmed. Diammoniate of diborane $B_2H_6 \cdot 2NH_3$ was prepared by adding 1.035 mmoles of diborane to frozen ammonia in the same manner in which normal diammoniate is normally prepared. After the diborane had been taken up by the ammonia, the excess ammonia was sublimed from the system at -45°C instead of -78°C over a period of 12 hours. Ammonia was then returned and the resulting solution was aged at -45° for around 18 hours.

The molecular weight of the above product was determined from the vapor-pressure depression of the ammonia solution. Results, shown in Fig. 1, confirm the earlier observations of Schultz for this compound and are consistent, within limits, with the formula $[HB(NH_3)_3][BH_4]_2$ for the product.

B. COMPOUND PREPARATION

H_3BNH_3 and the conventional $B_2H_6 \cdot 2NH_3$, $[H_2B(NH_3)_2][BH_4]$ have been prepared for further study.

C. STUDIES ON THE AMMONOLYSIS OF BH_2NH_2 FROM THE RESIDUES OF THE ALKALI METAL
$B_2H_6 \cdot 2NH_3$ REACTION

Reports by Schaeffer, Adams, and Koenig[2] and independent observations in this laboratory[3] indicated that the solid residues from the alkali metal-

1. R. W. Parry, G. Kodama, and D. R. Schultz, Final Report, Project 1966, Eng.
   Res. Inst., Univ. of Mich., June, 1956, p. 90.

2. G. W. Schaeffer, M. D. Adams, and F. J. Koenig, S.J., J. Am. Chem. Soc., 78,
   725 (1956).

3. S. G. Shore and R. W. Parry, Final Report, Project 1966, Eng. Res. Inst.,
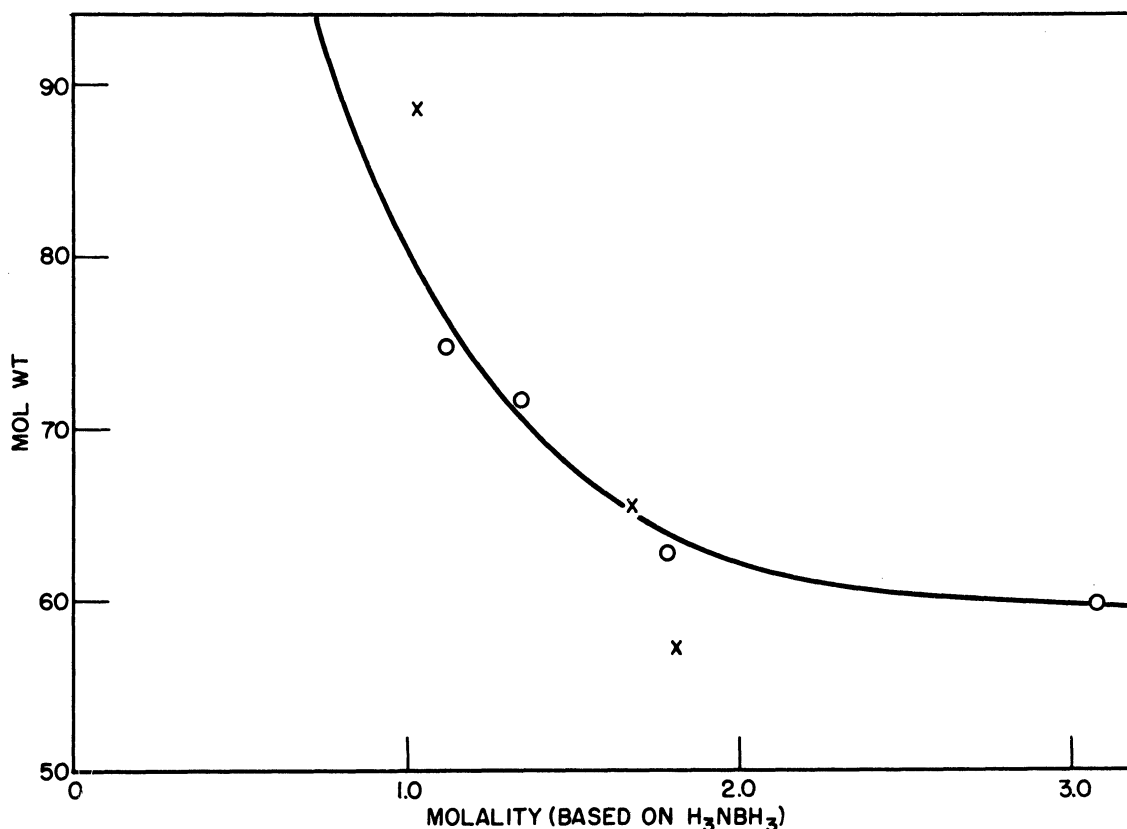   Univ. of Mich., June, 1956, p. 73.

Fig. 1. The apparent molecular weight in liquid ammonia
of $B_2H_6 \cdot 2NH_3$ prepared at $-45°C$ instead of $-78°C$.

diammoniate reaction (i.e., BH_2NH_2 and MBH_4) reacted with ammonia at room tem-
perature to give off H_2. A tracer study[3] showed that such hydrogen arises from
the interaction of a hydridic boron-hydrogen unit and a protonic nitrogen-
hydrogen unit. Schaeffer, Adams, and Koenig[2] assigned the equation

$$H_2BNH_2 + NH_3 \longrightarrow HB(NH_2)_2 + H_2$$
$$\xrightarrow{NH_3} B(NH_2)_3 + H_2$$
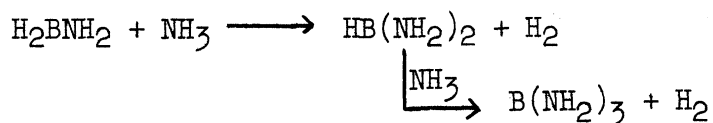
to the process, but several features of such a simple, direct process are open
to question. In the first place, the ready reaction between the very slightly
acidic ammonia and the residue H_2BNH_2 seems inconsistent with the properties
expected for H_2BNH_2. The formally analogous compound $[H_2BNHCH_3]_3$ will float on
a slightly acidic water solution at room temperature with only very slow hy-
drolysis. Complete hydrolysis is effected only by a boiling 20% hydrochloric
acid solution. It is difficult to understand why replacement of a hydrogen on
the nitrogen by a methyl group should cause such a decrease in the hydridic
character of the hydrogens bound to boron that H_2BNH_2 would react with ammonia
at room temperature, whereas H_2BNHCH_3 would not react with cold aqueous acid at
room temperature.

Other observations are equally disturbing. Schaeffer, Adams, and Koenig[2] reported that the presence of an alkali metal borohydride promoted the reaction—$LiBH_4$ being very effective while KBH_4 was relatively ineffective. $NaBH_4$ occupied an intermediate position. Their interpretation of this observation seems to be based on the relative abilities of $LiBH_4$ and KBH_4 to hold ammonia in the reaction zone as the reaction temperature of the system was raised. A number of uncertainties in the foregoing observations and interpretations have prompted a more thorough study of the system H_2BNH_2-NH_3.

A mixture of H_2BNH_2 and KBH_4 in liquid ammonia was prepared by allowing $[H_2B(NH_3)_2][BH_4]$ to react with a slight excess of potassium in liquid ammonia. After reaction was complete all excess potassium was removed quantitatively by amalgamating with about 0.7 cc of liquid mercury at -35°C. The solution was filtered from the potassium-amalgam and the solvent was removed from the system at -78°. The mixture of pure KBH_4-H_2BNH_2 was transferred under nitrogen to a dry box where it could be weighed.

In a separate reaction vessel a sample (1.09 mmoles) of commercial $LiBH_4$ was attached to the vacuum line and dissolved in 1 cc of liquid ammonia. Hydrogen, which evolved very slowly, was measured. After 24 hours a sample consisting of about .07 mmole each of the KBH_4-H_2BNH_2 mixture was weighed out in a dry box and introduced into the system under dry nitrogen. The entire mass was dissolved in liquid ammonia, then the liquid phase was removed and the system was allowed to warm to room temperature in contact with gaseous NH_3. Data in Fig. 2 show that hydrogen evolution was extremely slow under these conditions, less than .018 mmole of H_2 being evolved from .07 mmole of H_2BNH_2 in 18 hours at room temperature.

If the explanation of Schaeffer, Adams, and Koenig[2] were correct, this system should have lost H_2 at an appreciable rate since H_2BNH_2, KBH_4, and a considerable excess of $LiBH_4$ were all present. As the data in Fig. 2 show, hydrogen evolution became extremely rapid after an excess of Na metal was introduced into the system; the entire solid was dissolved in liquid ammonia; then the liquid phase was removed and the solids were held at room temperature in contact with gaseous NH_3. Hydrogen corresponding to the reaction H_2BNH_2 + $NH_3 \longrightarrow HB(NH_2)_3 + H_2$ was evolved rapidly, while hydrogen corresponding to the second step evolved more slowly.

D. DISCUSSION

The foregoing observations suggest that it is not $LiBH_4$ which is responsible for the reaction between H_2BNH_2 and NH_3 at room temperature, but the alkali metal. When excess alkali metal was rigorously removed from the system by mercury extraction, H_2BNH_2 and $LiBH_4$ reacted very slowly with gaseous ammonia at room temperature. Addition of alkali metal accelerated the reaction in a dramatic fashion. The following explanation is consistent with all facts now available, including those from the tracer study, the work of Schaeffer, Adams, and Koenig, and the present investigation.
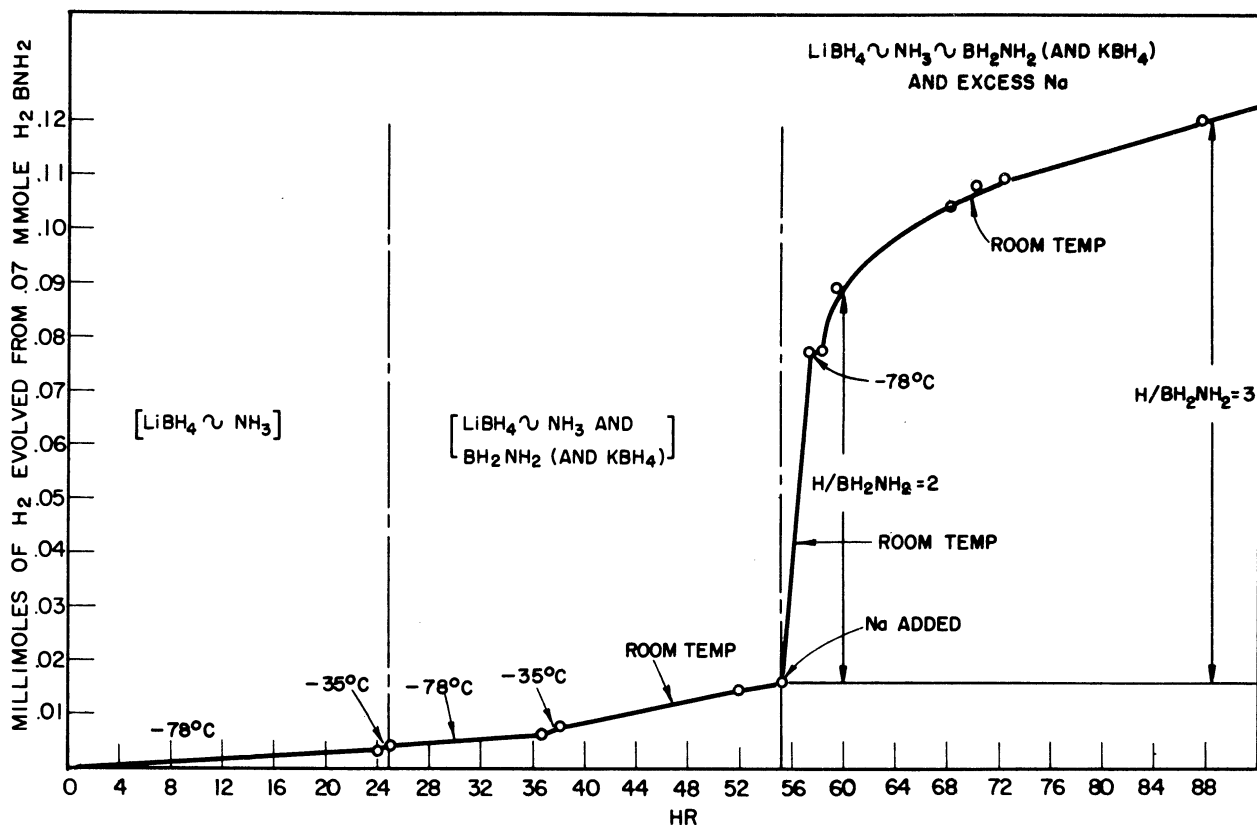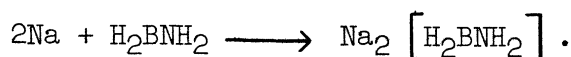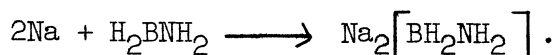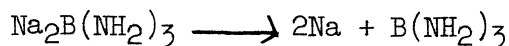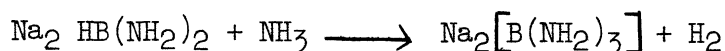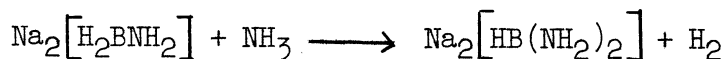
Fig. 2. Rate of H_2 evolution in system
H_2BNH_2-MBH_4 and alkali metal.

It is postulated that the free alkali metal in the system reacts with the H_2BNH_2 in accordance with the following equation to give a compound comparable to the "base" $Na_2[HB(CH_3)_2]$ described by Burg and Campbell:[4]

$$2Na + H_2BNH_2 \longrightarrow Na_2[H_2BNH_2].$$

Burg and Campbell found the hydrogen of their compound, $Na_2[HB(CH_3)_2]$, to be extremely hydridic in character. The compound reduced SiH_3Cl to SiH_4. They also found some evidence which can be interpreted as indicating ammonolysis of $Na_2[HB(CH_3)_2]$ at temperatures below -50°C. In view of these observations the compound $Na_2[H_2BNH_2]$ would be expected to be easily ammonolyzed at room temperature:

$$Na_2[H_2BNH_2] + NH_3 \longrightarrow Na_2[HB(NH_2)_2] + H_2$$

$$Na_2 HB(NH_2)_2 + NH_3 \longrightarrow Na_2[B(NH_2)_3] + H_2$$

$$Na_2B(NH_2)_3 \longrightarrow 2Na + B(NH_2)_3$$

$$2Na + H_2BNH_2 \longrightarrow Na_2[BH_2NH_2].$$

4. A. B. Burg and G. W. Campbell, Jr., J. Am. Chem. Soc., 74, 3744 (1952).

In accordance with the above sequence a small amount of alkali metal could well be catalytic for the hydrogen evolution.

If one recalls the fact that $LiBH_4$ is very proton sensitive, $NaBH_4$ less so, and KBH_4 stable even in water solution, it is not difficult to rationalize Schaeffer's observation regarding the relative ammonolysis rates for the residues resulting from the reaction of Li, Na, or K with $B_2H_6 \cdot 2NH_3$. The relative proton sensitivity of $Li_2(H_2BNH_2)$, $Na_2(H_2BNH_2)$, and $K_2(H_2BNH_2)$ would decrease quite rapidly from Li to K, hence the rate of the ammonolysis reaction would be expected to fall sharply, as was observed. Attempts to prepare pure $K_2\left[H_2BNH_2\right]$ are now in progress.

II. RAMAN SPECTRAL STUDIES

A. THE RAMAN SPECTRUM OF H_3BCO. FORCE CONSTANTS FOR THE CARBON MONOXIDE— BORANE MOLECULE

The vibrational frequencies (Raman) of the BH_3CO and BD_3CO molecules and the results of a normal coordinate treatment have been given in a previous report.[5] The calculations were carried out using the FG method of Wilson based on the use of symmetry coordinates which are linear combinations of the internal coordinates (bond lengths, bond angles, etc.) of the molecule. In ideal cases, the symmetry coordinates are close approximations to the actual normal coordinates. The force constants which are obtained most directly in this approach are the symmetry force constants related to the respective symmetry coordinates. Since these quantities are rather difficult to interpret in terms of the chemical behavior of the molecule, which one is accustomed to thinking of in terms of bonds and bond angles, the symmetry force constants are customarily resolved into the simpler valence force constants by making use of the original transformation between coordinates.

Frequently there are more valence force constants than symmetry coordinates so that one cannot resolve certain combinations of the valence force constants unless arbitrary assumptions are made. In the previous report,[5] the assumption was made that $k_{\alpha\alpha} = k_{\beta\beta}$, and the values tabulated for the valence force constants were derived on this basis.

An alternative procedure for resolving all combinations of force constants, which is more satisfactory, makes use of the fact that the sum of the changes in all the angles around an atom bonded to four others must be identically zero; that is, another (redundant) symmetry coordinate can be defined which must be identically zero. In the case of BH_3CO, this coordinate is

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5. R. W. Parry, G. Kodama, S. G. Shore, R. C. Taylor, and E. Alton, Quarterly Report No. 1, Project 2469, Eng. Res. Inst., Univ. of Mich., Jan.-Mar., 1956.

$$S_0 = (6)^{-1/2} (\Delta\alpha_{12} + \Delta\alpha_{23} + \Delta\alpha_{13} + \Delta\beta_1 + \Delta\beta_2 + \Delta\beta_3) \equiv 0.$$

By including this coordinate in the original transformation from valence to symmetry coordinates and equating the elements of the F (symmetry force constant) matrix belonging to this redundant coordinate to zero, additional relationships are obtained which allow values to be given to all valence force constants. These revised numbers are given in the table below.

VALENCE FORCE CONSTANTS FOR THE BH_3CO MOLECULE

Force Constant	Value (Millidynes/Angstrom)
k_T	17.9800
k_R	2.7875
k_r	3.1607
k_α	0.2799*
k_β	0.2644*
k	0.2744
k_{rr}	0.0687
$k_{\alpha\alpha}$	0.0365*
$k_{\beta\beta}$	0.0442*
$k_{\alpha\beta} = k'_{\alpha B}$	-0.1176*
$k_{R\beta}$	0.1451
$k_{R\alpha} = -k_{R\beta}$	-0.0726*
k_β	0.0647**

*revised

**error corrected

B. THE RAMAN SPECTRUM OF BH_4^-. FORCE CONSTANTS FOR THE BOROHYDRIDE ION

Using the frequency assignments reported recently[6] for the BH_4^- and BD_4^- ions dissolved in liquid ammonia, force constants have been calculated using the general quadratic valence force potential function below:

$$2V = k_r \sum \Delta r_i^2 + 2k_{rr} \sum \Delta r_i \Delta r_j + r^2 k_\alpha \sum^{i \neq j} \Delta\alpha_{ij}^2 + 2r^2 k_{\alpha\alpha} \sum \Delta\alpha_{ij}\Delta\alpha_{jk}$$

$$+ 2r^2 k'_{\alpha\alpha} \sum \Delta\alpha_{ij}\Delta\alpha_{kl} + 2r\, k_{r\alpha} \sum \Delta r_i \Delta\alpha_{ij} + 2r\, k'_{r\alpha} \sum \Delta r_i \Delta\alpha_{jk}.$$

6. R. C. Taylor, A. E. Emery, and D. R. Schultz, Final Report, Project 1966, Eng. Res. Inst., Univ. of Mich., June, 1956, p. 92.

Principal force constants in the above are indicated by a single index and interaction constants by a double index; those constants relating two coordinates having only a single atom in common are indicated by a prime.

The numerical values for the constants are tabulated in Table I and are compared with the appropriate values of the force constants previously reported for the BH_3CO molecule.[5] The observed and calculated frequencies are given in Table II.

TABLE I

FORCE CONSTANTS FOR THE BOROHYDRIDE ION IN LIQUID
AMMONIA SOLUTIONS (IN MILLIDYNES/ANGSTROM)

Force Constant	Value	Comparable BH_3CO Value
k_r	2.751	3.161
k_α	0.241	0.280
k_{rr}	0.0763	0.0687
$k_{\alpha\alpha}$	-0.0484	0.0365
$k'_{\alpha\alpha}$	-0.0471	$-0.1176 = k'_{\alpha\beta}$
$k_{r\alpha}$	0.0550	0.0
$k'_{r\alpha}$	-0.0550	0.0

TABLE II

OBSERVED AND CALCULATED FREQUENCIES FOR THE BOROHYDRIDE
ION IN LIQUID AMMONIA SOLUTION

Frequency			Observed	Calculated	Diff.	% Diff.
BH_4^-	ν_1	A_1	2264 cm^{-1}	2241 cm^{-1}	-23	-1.02%
	ν_2	E	1205	1212	7	0.58
	ν_3	F_2	2239	2238	- 1	-0.04
	ν_4	F_2	(1085)	1086	1	0.09
BD_4^-	ν_1	A_1	1568	1585	17	1.08
	ν_2	E	862	857	- 5	-0.58
	ν_3	F_2	1665	1666	1	0.06
	ν_4	F_2	827	822	- 5	-0.60

(The frequency enclosed in parentheses was not directly observed as a fundamental but was obtained from the overtone.)

Standard deviation of eight frequencies = 0.6%.

The agreement between observed and calculated values in general is quite satisfactory, except possibly for the A_1 frequencies. The nature of the disagreement in the latter case perhaps is best discussed by noting that the frequency ratio of the hydrogen to the deuterium vibration is 1.45 as compared to the theoretical harmonic value of 1.41. Since the normal effect of an-harmonicity is to cause the observed ratio to be less than the harmonic value, it is possible that one of the observed frequencies has been disturbed by res-onance with an overtone or combination of the other fundamentals. It is hoped that this point can be clarified by using isotopically pure B^{10} in the boro-hydride ions and liquid ND_3 as the solvent.

It is of interest to note that the B-H force constant is some 10-15% less in the borohydride ion than it is in the carbon monoxide—borane molecule. Since one would expect stronger bonding for a trigonal sp^2 hybridization than for the tetrahedral sp^3 configuration, the comparison indicates that the borane group in BH_3CO retains a significant amount of the trigonal character expected in free borane despite the contribution from the lone pair of electrons on the carbon. This conclusion is in accord with the larger than tetrahedal angle (113°) observed in BH_3CO.

Somewhat less information can be obtained from the other constants. The positive sign of the interaction constant, k_{rr}, indicates that as one B-H bond is stretched, the others tend to contract. This behavior is to be ex-pected if ionic repulsion between the hydrogen atoms is present. However, re-moval of a hydrogen would leave behind a BH_3 molecule with a trigonal sp^2 electronic configuration in which one would also expect shorter B-H bonds. Con-sequently, both the change in hybridization during a B-H stretching vibration and the coulombic interaction of the hydrogen atoms predict the same sign for the interaction term and one cannot determine conclusively which is dominant. Exactly similar arguments with the same conclusion can be applied in the case of the constants, $k_{r\alpha}$ and $k'_{r\alpha}$.

III. THE REACTIONS AND STRUCTURES
OF THE AMMONIA ADDITION COMPOUNDS OF B_4H_{10}

A. BACKGROUND

Conditions favoring either symmetrical or nonsymmetrical cleavage of the double bridge bond in B_4H_{10} are summarized in an earlier report.[5]

B. THE PREPARATION OF B_4H_{10}

Laboratory stocks of B_4H_{10} became exhausted and new stocks have been made by decomposition of B_2H_6 under pressure. The flow method described

by Burg and Stone[7] was used as well as the bomb method in which B_2H_6 under pressure was stored in a tank at room temperature. More B_4H_{10} is still being made.

C. THE REACTION BETWEEN B_4H_{10} AND NH_3

Additional data on the system ammonia-B_4H_{10} has been sought. A sample of B_4H_{10} was placed in a tube and increasing amounts of ammonia were added. The equilibrium pressure on the system was measured at -78°, -63°, -45°, and -35°C. Many days were allowed to reach equilibrium at each composition-temperature point. Data are presented in Fig. 3. The highest definite ammoniate appears to be $B_4H_{10} \cdot 6NH_3$ rather than $B_4H_{10} \cdot 7NH_3$ as previously reported.[5] This study is being continued. Equilibrium is approached very slowly in all cases.
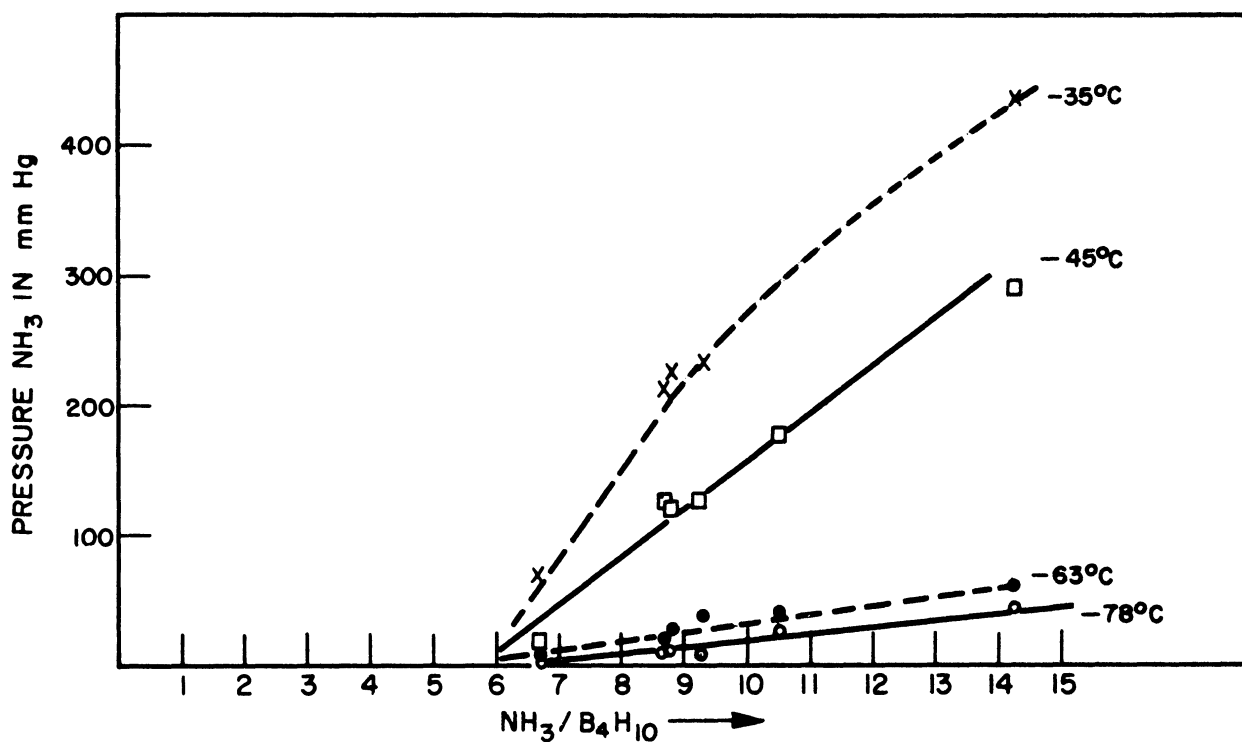

Fig. 3. The ammonia-B_4H_{10} system.

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7. A. B. Burg and F. G. A. Stone, J. Am. Chem. Soc. 75, 228 (1953).

## IV. THE REACTION BETWEEN Al_2Cl_6 AND PF_3

An earlier attempt by Chatt and Williams[8] to prepare an addition compound between PF_3 and $AlCl_3$ was made by passing PF_3 over sublimed $AlCl_3$ at a temperature of 250°C. No addition product was reported. More recently Holmes and Brown[9] reported that $AlCl_3$ would not combine with PCl_3 in a low-temperature study.

Earlier work in this laboratory[10] indicated that B_2H_6 at room temperature would combine with PF_3 under high pressure to give the unstable compound H_3BPF_3. BF_3 gave no evidence for interaction with PF_3 under comparable conditions. From these facts it was suggested that those Lewis acids which are dimeric in the free state would combine with very weak acids such as PF_3, whereas those which are monomeric [i.e., BF_3, $B(CH_3)_3$, etc.] would not. In an effort to test this prediction, the system Al_2Cl_6-PF_3 has been studied, using the methods employed in the B_2H_6-PF_3 study.

Very pure resublimed Al_2Cl_6 (99.9+% Al_2Cl_6) reacts with PF_3 in a bomb tube under 8 atmospheres pressure in accordance with the following equation:

$$Al_2Cl_6 + 2PF_3 \rightleftharpoons 2Cl_3AlPF_3 .$$
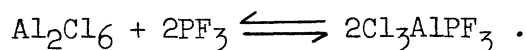
About 4 hours at room temperature was required for reaction. Shorter periods of time or lower pressures gave no reaction. Longer periods of time permitted group exchange on the complex
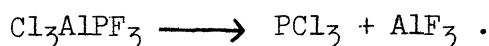
$$Cl_3AlPF_3 \longrightarrow PCl_3 + AlF_3 .$$

PF_3 and AlF_3 were recovered as products.

The identity of the complex Cl_3AlPF_3 was established by determining the amount of PF_3 combining with a given amount of Al_2Cl_6, then displacing PF_3 from an ether solution of the complex at -112°C, using trimethylamine. The amount of PF_3 recovered was equal to the amount of trimethylamine added, indicating the reaction

$$Cl_3AlPF_3 + NMe_3 \longrightarrow Cl_3AlNMe_3 + PF_3 .$$
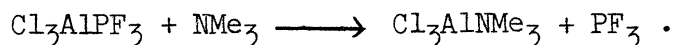
A formal report will be written to describe this work in more detail.

8. J. Chatt and A. A. Williams, J. Chem. Soc., 3061 (1951).

9. R. R. Holmes and H. C. Brown, Paper No. 70, Div. of Phys. and Inorg. Chemistry, Meeting of American Chemical Society, Dallas, Texas, April 12, 1956.

10. R. W. Parry and T. C. Bissot, J. Am. Chem. Soc., 78, 1524 (1956).