the π chemical shifts of the boron trihalides.[2] This gives the equation for the observed shift (in p.p.m.)

$$\delta = 480 - 201.5E_x + 1.79\delta_\pi \qquad (4)$$

The agreement between this equation and all of the BX_4^- chemical shifts which were measured can be seen in Figure 1, where $\delta_\sigma = \delta_{obsd} - 1.79\delta_\pi$. All of the alkyls have similar shifts to $B(CH_3)_4^-$ in this figure. The values of all of the parameters of interest are collected in Table I.

Some mention should be made of the observed chemical shift of the ion $B(C\equiv CC_6H_5)_4^-$ which has been reported.[18] A value of $+31.2$ p.p.m. shows an unusually high shielding of the boron nucleus considering that four sp carbons are attached to the boron. The electronegativity of an sp carbon atom has been calculated and a value of 3.29 reported,[19] which is even more electronegative than chlorine.

It is very likely that substituent electronegativity contributes to both the diamagnetic and paramagnetic shielding effects in the BX_4^- ions. It is of interest that those ions which deviate the most from a direct correlation with substituent electronegativity are also

(18) J. Hinze and H. H. Jaffé, *J. Am. Chem. Soc.*, **84**, 540 (1962).
(19) L. H. Meyer and H. S. Gutowsky, *J. Phys. Chem.*, **57**, 481 (1953).

those which have large π-bond contributions in the trigonal compounds. Several investigators[19–21] engaged in n.m.r. studies of saturated haloalkanes have invoked double-bond and no-bond structures. It would be more correct, perhaps, to describe the situation as a contribution to the total molecular wave function by low-lying antibonding orbitals which are usually ignored in a simple structural picture.[22,23] It is also likely, however, that a variety of effects caused by bond anisotropies and low-lying excited electronic states are important factors. It is not surprising that these are most prominent in the substituents which have π-orbital systems. A thorough understanding of the shifts in terms of actual calculations would be difficult.

A similar study of the Al^{27} chemical shifts in the analogous AlX_4^- ions is now being undertaken to determine the effects of the empty Al d orbitals.

(20) R. Livingston, *ibid.*, **57**, 496 (1953).
(21) R. S. Smith and E. A. Smith, *ibid.*, **63**, 1701 (1959).
(22) J. F. A. Williams, *Trans. Faraday Soc.*, **57**, 2089 (1961).
(23) G. Kohnstam, *J. Chem. Soc.*, 2066 (1960).

Contribution from the Department of Chemistry,
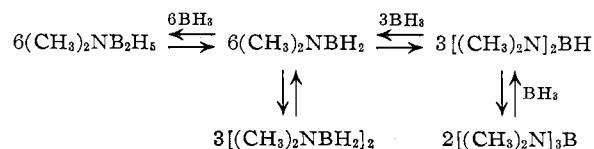University of Southern California, Los Angeles, California 90007

Lewis Acid–Base Reactions among Dimethylaminoboron Hydrides[1]
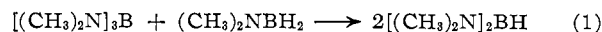
By ANTON B. BURG AND JAGTAR S. SANDHU

The dimethylaminoboron hydrides related to diborane form a system of Lewis acids and bases, the interconversion of which can be described as addition or removal of BH_3 groups. The first-stage action of $[(CH_3)_2N]_3B$ to remove BH_3 from $(CH_3)_2N \cdot BH_3$ is not appreciably reversible, but the second stage, in which $[(CH_3)_2N]_2BH$ and $(CH_3)_3N \cdot BH_3$ form $2(CH_3)_2NBH_2$ and $(CH_3)_3N$, is reversible with $\Delta F^\circ = 13.95 - 0.0330T$ kcal. Our base$\cdot(CH_3)_2NB_2H_5$ adducts show vapor-phase dissociation increasing in the order pyridine, $(CH_3)_3P$, 2-methylpyridine, $(CH_3)_3N$; and $(CH_3)_2PH \cdot (CH_3)_2NB_2H_5$ fails to exist in the vapor phase but forms a partially dissociated liquid. All five of these adducts on heating react further to form $(CH_3)_2NBH_2$ and base$\cdot BH_3$, without reversal. The adducts $CH_3PH_2 \cdot (CH_3)_2NB_2H_5$ and $(CH_3)_2PCF_3 \cdot (CH_3)_2NB_2H_5$ are still more easily dissociated, and their conversion to BH_3 complexes and $(CH_3)_2NBH_2$ is reversible with $\Delta F^\circ = 10.61 - 0.0268T$ and $6.59 - 0.01943T$ kcal., respectively. It is quite apparent that diborane is a much stronger Lewis acid than $(CH_3)_2NB_2H_5$.

Earlier studies of aminoboron hydrides[2,3] indicated the following pattern of acid–base reactions wherein amino groups exert a basic function while boron (here represented as a BH_3 group transferring hydride) accounts for Lewis acid action (eq. 1). In this pattern, of course, the BH_3 group is added in the direction of the nearest arrow.

$$6(CH_3)_2NB_2H_5 \;\underset{\longrightarrow}{\overset{6BH_3}{\rightleftarrows}}\; 6(CH_3)_2NBH_2 \;\underset{\longrightarrow}{\overset{3BH_3}{\rightleftarrows}}\; 3[(CH_3)_2N]_2BH$$

$$\Big\updownarrow \qquad\qquad\qquad \Big\updownarrow BH_3$$

$$3[(CH_3)_2NBH_2]_2 \qquad 2[(CH_3)_2N]_3B$$

Implicit in this system is the neutralization reaction

$$[(CH_3)_2N]_3B + (CH_3)_2NBH_2 \longrightarrow 2[(CH_3)_2N]_2BH \qquad (1)$$

which we now have found to be essentially irreversible. For a fuller study of the system, we have also used $(CH_3)_3N \cdot BH_3$ as a source of BH_3; and a series of bases having different strengths served to remove BH_3 from $(CH_3)_2NB_2H_5$; also, equilibrium constants were determined wherever feasible. Thus reaction 2, pre-

viously written as reversible,[3] proved not to be so at moderate pressures of $(CH_3)_3N$; however, reaction 3 could be equilibrated in the range 83–127°, leading by

$$2[(CH_3)_2N]_3B + (CH_3)_3N \cdot BH_3 \longrightarrow 3[(CH_3)_2N]_2BH + (CH_3)_3N \quad (2)$$

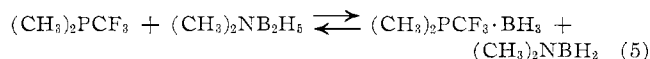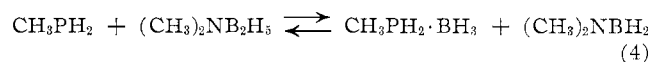$$[(CH_3)_2N]_2BH + (CH_3)_3N \cdot BH_3 \rightleftharpoons 2(CH_3)_2NBH_2 + (CH_3)_3N \quad (3)$$
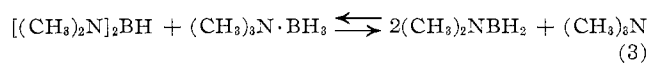
extrapolation to $\Delta F° = 4.11$ kcal. at 298°K.

The irreversibility of processes 1 and 2 would correlate with the extreme base character of $[(CH_3)_2N]_3B$, in which the mutual competition of $N \rightarrow B$ π bonding from three amino groups to one boron atom would leave each nitrogen atom with much of its normal electron-donor strength toward Lewis acids. This situation has been thoroughly studied by Skinner and Smith in relation to the conversion of $[(CH_3)_2N]_3B$ to aminoboron chlorides by action of BCl_3.[4] They found that the B–N bond strength is quite decidedly increased as Cl replaces $(CH_3)_2N$, meaning that the $N \rightarrow B$ π bonding is weakened by any adjacent $(CH_3)_2N$ groups.

The direct dissociation of $(CH_3)_2NB_2H_5$ to $(CH_3)_2NBH_2$ and B_2H_6 was observed in our laboratories by Dr. W. A. G. Graham in December 1956. He evaporated the sample *in vacuo* from a trap at −78 or −64° and passed the low-pressure vapor through a Pyrex tube at 250 or 300°. The material trapped at −196° included B_2H_6, $(CH_3)_2NBH_2$, and a trace of $[(CH_3)_2N]_2BH$; and there was major recovery of $(CH_3)_2NB_2H_5$. The results could have only qualitative value, for the pressure and residence time of the material passing through the hot tube could not be estimated. Also, some irreversible decomposition, forming hydrogen and nonvolatile products, further discouraged any attempt to judge the equilibria.

For another approach to this dissociation, we tried the action of various bases. It had been known that $(CH_3)_2NB_2H_5$ would form the adduct $(CH_3)_3N \cdot BH_2[(CH_3)_2N]BH_3$,[2] the structure of which could be inferred in relation to earlier studies of $H_2NB_2H_5$,[5] and, in fact, this $N \rightarrow B–N \rightarrow B$ chain pattern has been confirmed quite recently.[6] We now have learned that this $(CH_3)_3N$ adduct and the similar adducts of $(CH_3)_2NB_2H_5$ with $(CH_3)_3P$, pyridine, and 1-methylpyridine all can exist in the vapor phase, with reversible dissociation. However, at elevated temperatures or sometimes even on long standing at room temperature, the irreversible second step occurs, to form base $\cdot BH_3$ and $(CH_3)_2NBH_2$.[2] The weaker base $(CH_3)_2PH$ reversibly forms the adduct $(CH_3)_2PH \cdot (CH_3)_2NB_2H_5$, for which the molecular weight shows complete dissociation in the vapor phase at 24 or 65°, while the Trouton constant suggests some dissociation in the liquid phase. Then on longer heating there is again the irreversible conversion to the BH_3 complex and $(CH_3)_2NBH_2$. The still weaker bases CH_3PH_2 and $(CH_3)_2PCF_3$

do not readily condense as adducts with $(CH_3)_2NB_2H_5$ at 25°, but at considerably lower temperatures they form definite 1:1 adducts having dissociation pressures not far lower than the volatility of $(CH_3)_2NB_2H_5$; apparently the energy of condensation must be evolved to stabilize them. Then for the reactions

$$CH_3PH_2 + (CH_3)_2NB_2H_5 \rightleftharpoons CH_3PH_2 \cdot BH_3 + (CH_3)_2NBH_2 \quad (4)$$

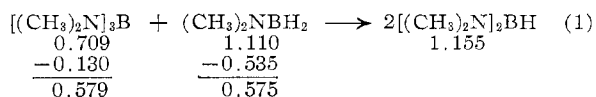$$(CH_3)_2PCF_3 + (CH_3)_2NB_2H_5 \rightleftharpoons (CH_3)_2PCF_3 \cdot BH_3 + (CH_3)_2NBH_2 \quad (5)$$

the equilibrium constants in the range 38–65° give $\Delta F° = 2.62$ and 0.795 kcal., respectively, at 298°K. Finally, it was found as expected that 2,6-dimethylpyridine would not react at all with $(CH_3)_2NB_2H_5$, since the methyl groups would prevent effective bonding from the ring nitrogen to boron. It is somewhat more surprising that little steric hindrance could be demonstrated for the case of 2-methylpyridine, in which the one methyl group might be expected to bend the $N \rightarrow B$ bond.

The experimental studies described in the following sections were performed by means of a high-vacuum manifold, whereby chemical processes could be investigated in a quantitative manner, often by separating components by the fractional condensation method. When this method failed to yield pure fractions, the impurities could be closely estimated by the intensities of their characteristic infrared bands, using a Beckman IR7 instrument for accurate comparison with known samples; or for quite irresolvable fractions, one component could be removed by a specific quantitative chemical process. For all such quantitative work it was usual to employ a series of U-traps and mercury float valves, avoiding as well as possible any contact with stopcock greases.

Reactions of the Triamide

Equation 1.—The process represented by the following equation (with quantities in mmoles, and minus signs to show recovery of reactants) occurred in a small sealed tube during 96 hr. at 98°.

$$\begin{array}{ccccc} [(CH_3)_2N]_3B & + & (CH_3)_2NBH_2 & \longrightarrow & 2[(CH_3)_2N]_2BH \quad (1) \\ 0.709 & & 1.110 & & 1.155 \\ \underline{-0.130} & & \underline{-0.535} & & \\ 0.579 & & 0.575 & & \end{array}$$

The incomplete character of this reaction is ascribed to a slow rate rather than an approach to equilibrium, in view of another experiment in which 1.003 mmoles of $[(CH_3)_2N]_2BH$, 0.005 mmole of $(CH_3)_2NBH_2$, and 0.310 mmole of $[(CH_3)_2N]_3B$ were heated together for 102 hr. at 100°. Then the infrared spectrum of the $[(CH_3)_2N]_2BH$ fraction showed no evidence of the strong 960 cm.$^{-1}$ band of $(CH_3)_2NBH_2$, at a sample pressure of 28 mm. and with path length 10 cm. This means that the upper limit of the $(CH_3)_2NBH_2$ impurity was 0.3%.

This sample of $[(CH_3)_2N]_2BH$ had been completely freed of $[(CH_3)_2N]_3B$ by high-vacuum distillation from a trap at −45°, and with the elimination of $(CH_3)_2NBH_2$ it must have been the purest sample yet achieved.

(4) H. A. Skinner and N. B. Smith, *J. Chem. Soc.*, 2324 (1954).

(5) H. I. Schlesinger, D. M. Ritter, and A. B. Burg, *J. Am. Chem. Soc.*, **60**, 2297 (1938).

(6) G. A. Hahn and R. Schaeffer, *ibid.*, **86**, 1503 (1964).

It melted quite sharply at $-55.4 \pm 0.2°$ and was appreciably more volatile than the previous "best sample,"[3] as shown by the data of Table I.

This pure sample was heated under conditions comparable to the initial experiment (112 hr., 98°) and then still showed no trace of the 960 cm.$^{-1}$ infrared band of $(CH_3)_2NBH_2$ in the 10-cm. cell at 28 mm. Hence reaction 1 was not appreciably reversed. It is judged that the negative free energy of process 1 is not less than 8 kcal. at 100°.

TABLE I
Volatility of Pure $[(CH_3)_2N]_2BH$

Log P = 6.4061 + 1.75 log T – 0.005566T – 2246/T
t_{760} = 105.7°; Trouton constant = 21.1 e.u.

Temp., °C.	0.30	6.67^a	20.05^a	28.30	40.08^a	68.39^a
P_{obsd}, mm.	8.60	12.71	27.01	41.33	72.43	230.38
P_{calcd}, mm.	8.61	12.71	27.00	41.33	72.43	230.42

^{a} Regional averages along the curve of log P vs. 1/T.

Equation 2.—A 3.391-mmole sample of $[(CH_3)_2N]_3B$ was completely consumed by heating with 2.298 mmoles of $(CH_3)_3N \cdot BH_3$ in a 305-ml. bulb for 36 hr. at 115°. The products were 2.055 mmoles of $(CH_3)_3N$, 4.685 mmoles of $[(CH_3)_2N]_2BH$, and 0.732 mmole of $(CH_3)_2$-NBH_2, showing that the second-stage process (3) had made some progress; indeed the experiment was analogous to a titration past the first stage of neutralization of a polyfunctional base: the presence of $(CH_3)_2$-NBH_2 assured the absence of the triamide.

For a more direct demonstration of the difficulty of reversing process 2, 1.130 mmoles of $(CH_3)_3N$ and 0.544 mmole of pure $[(CH_3)_2N]_2BH$ were heated together in a 552-ml. bulb for 13 days at 115°, producing no detectable trace (i.e., less than 0.005 mmole) of the triamide. The recovery of $(CH_3)_3N$ was 1.127 mmoles, suggesting a 0.3% mechanical loss. The earlier indication of the reversal of process 2 was based upon the liquid phase, with a far higher pressure of trimethylamine.[3]

The Energetics of Process 3

Equilibrium constants for the vapor-phase reaction of $(CH_3)_3N \cdot BH_3$ with $[(CH_3)_2N]_2BH$ to form $2(CH_3)_2$-NBH_2 with liberation of $(CH_3)_3N$ were sought in 15 experiments in which either the reactants or the products were heated in sealed bulbs at five different temperatures for periods as long as 3 weeks. The bulbs were immersed in oil baths with the temperatures constant to 0.2° or better. The adequacy of equilibration was confirmed by the results of both the forward and the reverse approaches at each temperature. After equilibration, each mixture was brought into the high-vacuum system for separation of the components as thoroughly as possible by distillation methods: thus $(CH_3)_3N$ was the only component which easily passed a trap at −78° and $(CH_3)_3N \cdot BH_3$ was easily trapped out as the least volatile component. The major part of the $(CH_3)_2NBH_2$ could be isolated in pure form, but since the remainder could not quite be removed from the $[(CH_3)_2N]_2BH$ fraction, the amount of it in that fraction was determined by the intensity of its 960 cm.$^{-1}$ infrared band, while the amount of $[(CH_3)_2N]_2BH$ in the cell was confirmed by the intensity of its unique band at 880 cm.$^{-1}$. Numerous other experiments had shown that the 960 cm.$^{-1}$ band offers a true measure of the total $(CH_3)_2NBH_2$, little affected by shifts in the monomer–dimer equilibrium.

The calculation of the equilibrium constants from the data required application of the previously-determined equation log K_{atm} = 11.126 − 4533/T for the dissociation of the dimer $[(CH_3)_2NBH_2]_2$.[3] Thus from the calculated K value and the total $(CH_3)_2$-NBH_2 it was possible to compute the partial pressure of the monomer $(CH_3)_2NBH_2$ for use in computing K for the present equilibrium. It was not necessary to correct for the disproportionation of $(CH_3)_2NBH_2$ into $[(CH_3)_2N]_2BH$ and $(CH_3)_2NB_2H_5$, since no appreciable amount of the latter could exist in the presence of $(CH_3)_3N$. Also unnecessary was any correction for the existence of the complex $(CH_3)_3N \cdot (CH_3)_2NBH_2$ in the vapor phase, for the earlier evidence for its vapor-phase existence[3] now seems misleading. Although a hot mixture of $(CH_3)_3N$ and $(CH_3)_2NBH_2$, suddenly quenched by liquid nitrogen, would deliver some of the $(CH_3)_2NBH_2$ with $(CH_3)_3N$ through a high-vacuum trap at −60°, which normally would condense out all $(CH_3)_2NBH_2$ as the dimer, the reason could be that the suddenly-quenched mixture contained monomeric $(CH_3)_2NBH_2$ which would not dimerize fast enough for condensation from the vapor phase as the mixture passed through the −60° trap. However, the condensation of $(CH_3)_3N$ with $(CH_3)_2NBH_2$ at −78° would imply formation of the 1:1 complex, since the amine alone would not be held at that temperature. In the present work, any allowance for this 1:1 complex in the vapor phase led only to inconsistent results. In particular, when it was assumed that all $(CH_3)_3N$ found in the −78° trap represented 1:1 complex which had existed as such in the vapor phase, the effect was to indicate an actual decrease of entropy as reaction 3 produced more molecules.

Correcting then only for the dimerization of $(CH_3)_2$-NBH_2, and using the definition $K = P_m^2P_a/P_cP_b$, for the partial pressures P in atmospheres and with m referring to monomeric $(CH_3)_2NBH_2$, a to free amine, c to $(CH_3)_3N \cdot BH_3$, and b to $[(CH_3)_2N]_2BH$, the mean K values were as shown in Table II.

TABLE II
Equilibria for Process 3

log K = 7.204 − 3046/T; $\Delta F°$ = 13,950 − 33.0T cal.

Temp., °C.	82.5	102	114	120	127
K_{obsd}, atm.	0.0436	0.115	0.216	0.295	0.388
K_{calcd}, atm.	0.0436	0.122	0.217	0.286	0.391

Attempts to equilibrate similar mixtures at 160° led to K values decidedly lower than calculated from the van't Hoff equation, apparently on account of side reactions leading to observed nonvolatile products. This now seems to be the chief reason for the failure of earlier attempts to study equilibria for process 3.

Dimethylaminodiborane with Various Bases

The Strong-Base Reactions.—The volatility behavior of the $(CH_3)_2NB_2H_5$ complexes of five strong bases, shown in Tables III–VII, was so consistent and so reproducible after recooling as to demonstrate the absence of the secondary processes forming base·BH_3 and the more volatile $(CH_3)_2NBH_2$ at temperatures within the tabulated ranges. However, upon evaporation each of the complexes was extensively dissociated (presumably into the original components), as shown by the pressures registered in known volumes by known quantities of the materials near their saturation pressures at room temperature. These results, shown with the melting points in Table VIII, demonstrate the order of decreasing base strength toward $(CH_3)_2NB_2H_5$

TABLE III
VOLATILITY OF SOLID $C_5H_5N\cdot(CH_3)_2NB_2H_5$

$\log P = 8.945 - 2929/T;\quad \Delta H_{vap} = 13.41$ kcal.

Temp., °C.	24.5	30.0	43.2	50.0	60.0	65.0
P_{obsd}, mm.	0.13	0.20	0.49	0.76	1.41	1.92
P_{calcd}, mm.	0.13	0.19	0.49	0.76	1.42	1.92

TABLE IV
VOLATILITY OF SOLID $(CH_3)_3P\cdot(CH_3)_2NB_2H_5$

$\log P = 8.769 - 2740/T;\quad \Delta H_{vap} = 12.54$ kcal.

Temp., °C.	21.1	26.0	32.9	35.8	45.4	57.0
P_{obsd}, mm.	0.27	0.42	0.66	0.80	1.46	2.96
P_{calcd}, mm.	0.29	0.41	0.66	0.80	1.47	2.95

TABLE V
VOLATILITY OF SOLID $1\text{-}CH_3C_5H_4N\cdot(CH_3)_2NB_2H_5$

$\log P = 9.716 - 2950/T;\quad \Delta H_{vap} = 13.50$ kcal.

Temp., °C.	24.0	25.7	28.7	36.2	40.4
P_{obsd}, mm.	0.59	0.70	0.90	1.52	2.01
P_{calcd}, mm.	0.61	0.70	0.88	1.51	2.03

TABLE VI
VOLATILITY OF SOLID $(CH_3)_3N\cdot(CH_3)_2NB_2H_5$

$\log P = 8.586 - 2318/T;\quad \Delta H_{vap} = 10.61$ kcal.

Temp., °C.	5.0	12.5	20.0	28.0	35.0
P_{obsd}, mm.	1.79	2.93	4.82	8.0	11.0
P_{calcd}, mm.	1.79	2.96	4.78	7.7	11.6

TABLE VII
VOLATILITY OF LIQUID $(CH_3)_2PH\cdot(CH_3)_2NB_2H_5$

$\log P = 9.978 - 2743/T;\quad$ Trouton constant $= 32.5$ e.u.

Temp., °C.	19.8	25.2	32.6	35.2	40.6	46.8
P_{obsd}, mm.	4.12	6.12	10.18	12.1	17.2	25.4
P_{calcd}, mm.	4.12	6.09	10.16	12.1	17.2	25.4

TABLE VIII
VAPOR PHASE DISSOCIATION OF THE ADDUCTS

Formula	M.p., °C.	Temp., °C.	P, mm.	Dissocn., %	$10^3 K$, atm.
$C_5H_5N\cdot(CH_3)_2NB_2H_5$	64.0	25.0	0.125	54	0.07
$(CH_3)_3P\cdot(CH_3)_2NB_2H_5$	74.5	24.5	0.28	55	0.16
$2\text{-}CH_3C_5H_4N\cdot(CH_3)_2NB_2H_5$	68.0	28.5	0.85	83	2.5
$(CH_3)_3N\cdot(CH_3)_2NB_2H_5$	33.9	24.0	5.00	76	9.0
$(CH_3)_2PH\cdot(CH_3)_2NB_2H_5$	9.0	24.0	5.62	100	...

as a Lewis acid, measured inversely by the dissociation constants K. The 0.5°-sharp melting points indicate again the absence of reactions other than dissociation.

For each of the three lowest pressures, as many as ten measurements were averaged to give a result dependable to 0.01 mm. Nevertheless, the interpretation of the K values probably is made uncertain by unknown and variant van der Waals effects. Thus only a rough comparison is valid.

It is interesting that the ΔH_{vap} values (correlating with the enthalpy of dissociation) for the 1-methylpyridine and pyridine complexes are nearly the same. Then if we assume that the vaporization of the undissociated complexes would cost about the same ΔH, it seems that the effect of steric hindrance by the methyl group in 1-methylpyridine is nearly compensated by the base-strengthening inductive effect of that methyl group. Noting that the constant terms of the $\log P$ equations represent entropy, it seems that the lower stability of the 1-methylpyridine complex is due to a considerably larger entropy of dissociative vaporization.

The low melting point of $(CH_3)_2PH\cdot(CH_3)_2NB_2H_5$ may well relate to partial dissociation in the liquid phase, for the Trouton constant should be higher than 32.5 if ΔH_{vap} included the full molar enthalpy of dissociation.

For comparison of the temperatures required for the irreversible conversion of these five adduct-equilibrium systems to base·BH_3 and $(CH_3)_2NBH_2$, we may roughly define as observable a rate of conversion requiring 20 min. to form an amount of $(CH_3)_2NBH_2$ detectable by an increase of vapor tension and confirmed by the 960 cm.$^{-1}$ infrared band. Then for the pyridine system the required temperature is near 70°; for trimethylphosphine, 57°; for 1-methylpyridine, 55°; and for trimethylamine, 37°. Thus the temperature requirement seems to increase with the bonding strength of the base, although the close similarity of the trimethylphosphine and 1-methylpyridine systems would not correlate with their very different dissociation constants. The dimethylphosphine system deviates extremely from the trend, for its temperature of incipient conversion is near 55°. Major conversion of this liquid–vapor system was observed after 8 hr. at 65°, leading to the 10 mm. vapor tension of $(CH_3)_2$-NBH_2 at 25°. Reversal of the conversion seemed more likely for this system than for the others, but a mixture of 1.05 mmoles of $(CH_3)_2PH$ and 1.10 mmoles of $(CH_3)_2$-NBH_2, heated for 30 hr. at 70°, yielded no $(CH_3)_2PH$. Hence the formation of 0.05 mmole of $(CH_3)_2NB_2H_5$ is ascribed only to the previously-noticed disproportionation of $(CH_3)_2NBH_2$.[3]

The Weak-Base Reactions.— The weak bases CH_3-PH_2 and $(CH_3)_2PCF_3$ have similar strengths of attachment to $(CH_3)_2NB_2H_5$, as shown by the data of Tables IX and X. Both adducts dissociate completely in the vapor phase, and in each case the partial pressure of each component (base or aminodiborane) is less than the vapor tension of that component at the same temperature; hence an equimolar escape of the two components into the vapor phase might be assumed. However, the two components of each system might have different solubilities in the liquid phase, where

TABLE IX

DISSOCIATION PRESSURES OF $CH_3PH_2 \cdot (CH_3)_2NB_2H_5$

Solid: $\log P = 10.600 - 2332/T$ Liquid: $\log P = 9.610 - 2071/T$

(m.p. $-9.5°$ calcd.; $-13.0°$ obsd.) (Trouton const. = 30.8 e.u.)

Temp., °C.	P_{obsd}, mm.	P_{calcd}, mm.	Temp., °C.	P_{obsd}, mm.	P_{calcd}, mm.
-63.5	0.30	0.30	-11.9	48.1	48.2
-60.5	0.45	0.44	-7.8	64.0	63.9
-51.7	1.18	1.18	-5.0	77.0	77.1
-41.8^a	3.29	3.31	0.00	107.2	106.8
-29.9^a	10.31	10.32	5.3	148.6	149.0
-21.65^a	21.30	21.28	12.0	222.7	222.7
-16.75	32.01	32.00			

^{a} Averages of $1/T$ and $\log P$.
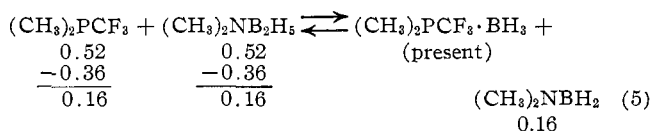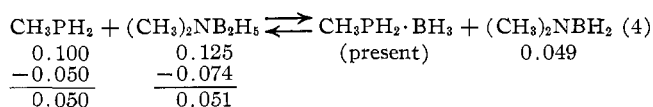
TABLE X

DISSOCIATION PRESSURES OF $(CH_3)_2PCF_3 \cdot (CH_3)_2NB_2H_5$

Solid: $\log P = 12.290 - 2766/T$ Liquid: $\log P = 9.180 - 1974/T$

(m.p. $-19.5°$ calcd.; $-16.7°$ obsd.) (Trouton const. = 28.8 e.u.)

Temp., °C.	P_{obsd}, mm.	P_{calcd}, mm.	Temp., °C.	P_{obsd}, mm.	P_{calcd}, mm.
-49.0	0.90	0.89	-15.2	33.90	33.89
-42.5	1.99	1.99	-9.0	51.25	51.29
-40.5	2.50	2.52	-5.0	66.08	66.08
-35.5	4.48	4.48	-0.20	88.71	88.72
-32.0	6.62	6.61			
-27.8	10.38	10.40			
-21.9	19.1	19.1			

they would be in equilibrium with the adduct. Such liquid-phase dissociation equilibria are strongly suggested by Trouton constants far lower than twice the normal 21 e.u. for pure unassociated liquids. It is more difficult to decide whether the solid phases here are pure adducts or contain equilibrium amounts of the components in solid solution: the very sharp melting points (0.2° ranges, but deviating from the calculated values) would not decide this question. Hence the volatility equations are not directly convertible to significant free energies.

The second-stage reactions 4 and 5 were explored in experiments summarized by the mmole quantities attached to the following equations, showing the extent of each reaction after heating at 55°: reaction 4 for 40 hr. in a 300-ml. bulb and reaction 5 for 12 hr. in a 500-ml. bulb. Here again the negative quantities of

$$CH_3PH_2 + (CH_3)_2NB_2H_5 \rightleftarrows CH_3PH_2 \cdot BH_3 + (CH_3)_2NBH_2 \quad (4)$$

0.100	0.125	(present)	0.049
-0.050	-0.074		
0.050	0.051		

$$(CH_3)_2PCF_3 + (CH_3)_2NB_2H_5 \rightleftarrows (CH_3)_2PCF_3 \cdot BH_3 +$$

0.52	0.52	(present)
-0.36	-0.36	
0.16	0.16	

$$(CH_3)_2NBH_2 \quad (5)$$
0.16

reactants represent recovery after the incomplete reactions. The estimates of $(CH_3)_2NBH_2$ were confirmed by the intensity of its 960 cm.$^{-1}$ infrared band, and there never was enough $[(CH_3)_2N]_2BH$ for detection by its strong 880 cm.$^{-1}$ infrared band. For identification of $CH_3PH_2 \cdot BH_3$ it was sufficient to compare the sample with the previously reported properties.[7] The complex $(CH_3)_2PCF_3 \cdot BH_3$ was identified by com-

parison with an authentic sample, made directly from B_2H_6 and $(CH_3)_2PCF_3$, the latter having been made by the literature method.[8] The volatility of this adduct was as shown in Table XI.

TABLE XI

VOLATILITY OF LIQUID $(CH_3)_2PCF_3 \cdot BH_3$

$\log P = 4.9313 + 1.75 \log T - 0.003300T - 2259/T$

($t_{760} = 158°$; Trouton constant = 21.00 e.u.)

Temp., °C.	22.4	29.1	35.4	45.2	56.1	64.1
P_{obsd}, mm.	4.33	6.39	8.88	14.57	24.0	35.0
P_{calcd}, mm.	4.33	6.32	8.88	14.62	24.5	35.0

This adduct seemed stable up to 130° but during 24 hr. in a sealed tube at 140° it decomposed in two ways: destruction of the BH_3 group to liberate 0.60-$(CH_3)_2PCF_3$ and 0.60H_2 per mole, and destruction of the CF_3 group with formation of $[(CH_3)_2PBH_2]_3$ and very little HCF_3.

For a full study of the equilibria of reactions 4 and 5, mixtures of the reactants or of the products were kept in sealed bulbs of known volume, immersed in oil baths at fixed temperatures. The equilibration periods were planned for five to seven times as long as suggested by the exploratory experiments, and their effectiveness was confirmed by the agreement of the K values for the forward and reverse approaches to equilibrium. The components of each final mixture could be measured after resolution by high-vacuum fractional condensation. Thus CH_3PH_2 and $(CH_3)_2$-NB_2H_5 were easily separated and clearly identified; and the weights of mixtures of $(CH_3)_2NBH_2$ and CH_3-$PH_2 \cdot BH_3$ confirmed the extent of reaction in each case. The separation of $(CH_3)_2PCF_3$ from $(CH_3)_2NB_2H_5$ was more difficult; hence the $(CH_3)_2PCF_3$ was taken out as the BH_3 complex. Then to confirm the equilibrium yields of $(CH_3)_2PCF_3 \cdot BH_3$ and $(CH_3)_2NBH_2$, the less volatile fraction representing them was weighed and the $(CH_3)_2NBH_2$ was determined by its 960 cm.$^{-1}$ infrared band. Thus, although the determination of any two components would have been sufficient, the basis of each K value was doubly confirmed. As before, each actual pressure of monomeric $(CH_3)_2NBH_2$ was calculated from the total quantity by means of the known equation[3] and the bulb volume.

The K values shown in Tables XII and XIII are based upon definitions in terms of the equations as

TABLE XII

EQUILIBRIA FOR REACTION 4

$\log K = 5.853 - 2317/T;$ $\Delta F° = 10,608 - 26.80T$ cal.

Temp., °C.	42.23	47.5	53.5	56.6	65.0
K_{obsd}	0.0321	0.0421	0.0575	0.0671	0.1002
K_{calcd}	0.0318	0.0424	0.0576	0.0671	0.1003

TABLE XIII

EQUILIBRIA FOR REACTION 5

$\log K = 4.244 - 1439/T;$ $\Delta F° = 6,588 - 19.43T$ cal.

Temp., °C.	38.0	46.7	53.5	56.6	65.0
K_{obsd}	0.418	0.551	0.699	0.754	0.976
K_{calcd}	0.416	0.556	0.690	0.760	0.974

(7) A. B. Burg and R. I. Wagner, *J. Am. Chem. Soc.*, **75**, 3872 (1953).

(8) R. N. Haszeldine and B. O. West, *J. Chem. Soc.*, 3631 (1956).

written, so that each forward process is favored by an increase of entropy but resisted by an increase of enthalpy. Every K value represents an average of at least two experiments. The datum for 42.23° in Table XI represents an average of log K and $1/T$ at 38.8 and 46.7°.

Assignment of MC Stretching and MCN Bending Frequencies in Metal Cyanide Complexes[1]

BY LLEWELLYN H. JONES

Infrared spectra of the MC stretching and MCN bending vibrations of $Au(CN)_2Cl_2^-$ and $Au(CN)_2Br_2^-$ and of the ^{13}C and ^{15}N enriched species have been observed in the solid state. By comparing the results with the frequencies calculated for the isotopic species it is shown that the MCN bending frequency is at 456 cm.$^{-1}$ for the chloride and 455 cm.$^{-1}$ for the bromide, while the MC stretching frequency is at 430 and 431 cm.$^{-1}$, respectively. Because this reverses a previous assignment, new sets of force constants are calculated. By analogy the frequencies of $Au(CN)_2I_2^-$ and $Au(CN)_4^-$ are reassigned also, and new force constants are calculated.

Introduction

There are essentially four types of vibrations in metal–cyanide complexes which lie in three spectral regions. The CN stretching frequencies occur in the region 2000–2250 cm.$^{-1}$. The CMC bending frequencies are around 100 cm.$^{-1}$. The MC stretching and MCN bending frequencies are in the 300–600 cm.$^{-1}$ region and are not always in the same order. Thus, it is not always possible to make conclusive assignments of the MC stretching and MCN bending frequencies. For example, the transition metal hexacyanides show two strongly infrared-active frequencies in the region 300–600 cm.$^{-1}$; one in the region 300–420 cm.$^{-1}$ and the other in the region 450–600 cm.$^{-1}$. Nakagawa and Shimanonchi[2] have assigned the higher frequency as MC stretching and the lower as MCN bending. Jones[3] has preferred the opposite assignment.

Another example of ambiguity lies in the assignments of the MC stretching and MCN bending frequencies of the dicyanodihalo complexes of trivalent gold, $Au(CN)_2X_2^-$. For example, solid $KAu(CN)_2Cl_2$ shows strong infrared absorption bands at 456 and 430 cm.$^{-1}$.[4] The *trans*-$Au(CN)_2Cl_2^-$ ion has D_{2h} symmetry and one of these frequencies arises from the B_{2u} MC stretching vibration while the other arises from the B_{3u} MCN bending vibration. The choice between the two possibilities is not conclusive without further data. It was previously postulated[4] that the higher frequency arises from MC stretching because the resulting force constant solution appeared more reasonable. However,

careful studies of the frequencies of the material enriched in ^{13}C and in ^{15}N show that the assignment was in error and should be reversed. This paper describes the work which leads to this conclusion.

Results

Calculated Isotopic Shifts for Frequencies of Au-$(CN)_2Cl_2^-$.—From a cursory examination of the G matrices[4] one might expect that a change of carbon mass would have a much greater effect on the MC stretching frequency than a change in nitrogen mass. However, this is not the case. The isotopic shifts can be predicted accurately from a computer calculation. The force constants were calculated from the frequencies of the normal species. The G matrix was then changed appropriately for isotopic substitution and the expected frequencies were then calculated from the previously determined force constants (which are assumed invariant to isotopic substitution). Inasmuch as the available ^{13}C and ^{15}N had a considerable amount of the normal isotopic species present, we also calculated frequencies for the mixed [12]C–[13]C and [14]N–[15]N species. This, of course, required a reduction of symmetry from D_{2h} to C_{2v} and a calculation based on the C_{2v} irreducible representations. The MC stretching vibration falls under the A_1 representation of C_{2v} while the MCN bending vibration falls under B_2 of C_{2v}.

The results of the calculations are given in Table I. The two vibrational frequencies in question are called ν_{11} and ν_{10} in keeping with the nomenclature of ref. 4, even though for the monosubstituted species a different numbering system would be appropriate. From Table I it is apparent that the shifts are quite different for ν_{11} and ν_{14}, and, in fact, it should not be difficult to distinguish ν_{11} from ν_{14} by the pattern of frequencies of the isotopic species.

(1) This work was sponsored by the U. S. Atomic Energy Commission.
(2) I. Nakagawa and T. Shimanouchi, *Spectrochim. Acta*, **16**, 424 (1960).
(3) L. H. Jones, *Inorg. Chem.*, **2**, 777 (1963).
(4) L. H. Jones, *ibid.*, **3**, 1581 (1964). In this reference the figures given were 455 and 424 cm.$^{-1}$. More accurate measurements give 430 and 456 cm.$^{-1}$. Also in this reference there are some minor errors. F_{45} should equal $\sqrt{2}(F\alpha\beta' + F\alpha\beta'')$, and $G_{13,14}$ should equal $+2\mu_m\rho_2$. The calculated values for unobserved ν_{13} should be about 13% lower.