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Reactions of Borane (BH₃). III. Absolute Rates of Formation of the

Donor-Acceptor Adducts BH₃**PF**₃ and **BH**₃**N**(**CH**₃)₃¹

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Absolute rate constants for the reactions of free borane, BH₃, with phosphorus trifluoride, PF₃, and trimethylamine, N(CH₃)₃, have been directly measured by observing the formation of the two donor-acceptor adducts BH₃PF₃ and BH₃N(CH₃)₅, respectively. At 500°K and at a total pressure of 6 Torr (ca. 98% helium) the rate constant for the formation of BH₃PF₃ is 1.5×10^8 l./mol sec while the rate constant for the formation of BH₃N(CH₃)₆ is 1.1×10^9 l./mol sec. The former may not be the high-pressure limiting value while the latter is probably close to the high-pressure limiting rate constant. These results are briefly discussed in terms of presently held concepts of donor-acceptor reactions.

The process in which an electron-pair donor molecule interacts with a tricoordinate boron atom to form a stable adduct is not well understood³ despite qualitative correlations with some structural properties of both donor and acceptor.³⁻⁷ Among the factors considered to be important for promoting donor-acceptor reactions are electron withdrawing and donating substituents on the acceptor and donor, the ability of the planar tricoordinate acceptor molecule to distort to a pyramidal geometry, and the absence of highly bulky substituents on either species which would interfere with their close approach. Thermochemical studies of the reactions of boron trihalides with the donor molecule pyridine⁴ have demonstrated that acceptor strength parallels the ease of distortion of the acceptor molecule:^{4,8} $BBr_3 > BCl_3 > BF_3$. BF_3 was found to be the weakest acceptor among the boron trihalides which is consistent with its high planar rigidity resulting from substantial π bonding.^{8,9} Several kinetic studies of the reactions of BF₃ with the methylamines and ammonia have been carried out.^{7,10} The following order of rate constants was obtained for the reactions of BF₃ with (a) ammonia, (m) mono-, (d) di-, and (t) trimethylamine; $k_{\rm a} < k_{\rm m} <$ $k_t < k_d$. More recently, however, the variation of k_m/k_t with pressure has been reported and at high pressures it is apparent that $k_m > k_t$.¹¹ The last result is attributed to a steric effect.

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The significance of steric effects on donor-acceptor reactions is part of a more fundamental question, namely, the intermolecular distance at which attractive interaction sets in and its dependence on relative orientation. Mulliken's charge-transfer theory for such reactions¹² provides a basis for qualitatively discussing this problem in terms of structural properties. The effective range of attractive interaction is the intermolecular distance at which electron transfer from donor to acceptor occurs. This is inversely proportional to the difference between ionization potential of the donor and electron affinity of the acceptor. Long-range interactions would minimize steric effects and, with a given acceptor, one would expect a correlation with the ionization potential of the donor. With shorter range interactions steric effects would play a role.

Knowledge of the acceptor behavior of the reactive species BH_3 with a somewhat smaller and supposedly more flexible structure than $BF_3^{8,9}$ would be distinctly useful in furthering our understanding of these reactions. Consequently, we have compared the reactivity of BH_3 and BF_3 toward both the same donor and different donors.

Experimental Section

Technique. The apparatus consists of a fast-flow gas-phase reactor coupled to a mass spectrometer utilizing a modulated molecular beam sampling technique. Detailed descriptions appear elsewhere¹⁸⁻¹⁷ and here only one major modification will be described. The original solid rod on which the thermocouple was mounted and scanned along the reactor was replaced by a quartz tube through which gases are directly introducted into the reactor. This dual-purpose inlet tube and thermocouple probe can be scanned along the axis of the main flow tube as before. Its approximate size and geometry are shown schematically in relation to the main flow tube in Figure 1. The 2 mm i.d. and 3 mm o.d. tubing is drawn to a capillary tip on which the thermocouple is mounted. Several millimeters above the tip are located the three exit holes (ca. 1 mm diameter) through which gas enters the main flow stream. Full details appear elsewhere.¹⁶

In making kinetic measurements, partial pressures of BH_3CO or BH_3PF_3 , up to 100 mTorr with the reactor unheated, are introduced into the main helium flowstream. The pyrolysis of the BH_3 source gas in the decomposition zone (D) produces BH_3 which reacts in the reaction zone (R). Here, along with recombination to form diborane, association with suitable substrate species takes place. As they are not mutually too reactive, BH_3CO source gas and PF_3 substrate gas are metered through separate leaks and are mixed with the helium carrier gas before entering the decomposition zone. However, trimethylamine is known to react readily with both $BH_3CO^{18,19}$ and $BH_3PF_3^{20}$ and therefore was injected directly into the reaction zone through



Figure 1. Schematic diagram of the inlet probe. T is the temperature of the gas along the axis of the flow tube, D is the decomposition zone used to prepare BH₃ from BH₃PF₃ or BH₃CO, R is the reaction zone, and l is the distance between probe tip and the end of the flow tube.

the inlet probe, as shown in Figure 1. This allowed the study of the formation of BH_3NMe_3 from BH_3 and NMe_3 without major complications from side reactions. In addition, use of the probe enables one to vary the residence time of the amine in the reaction zone by varying distance *l* between the probe tip and the end of the flow tube. This feature is essential to the difference method discussed below.

A typical kinetic run consists of making three sets of measurements apart from the initial sensitivity calibrations. Initial pressures $(P)_0$ of source and substrate gases introduced at several assigned leak settings are measured with the reactor unheated, by means of their appropriate ion intensities. Two additional sets of measurements using the same leak settings are made alternately at the short (S) and long (L) profiles to yield sample partial pressures at the beginning $(P)_{s}$ and end $(P)_{\rm L}$ of the reaction zone, respectively.¹⁷ At the end of the long profile shown in Figure 1 products from the recombination zone are sampled and consist of borane adducts, diborane and unreacted BH3. Sample pressures at the beginning of this zone are measured at the short profile, which is set up by reproducing zone D close to the sampling leak. Pressures of amine or PFs substrate are those measured initially and do not change when the reactor is heated.

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The technique of injecting gaseous reactants into a flow stream through a fixed or movable inlet probe is one which has been described in conjunction with several kinetic studies.²¹⁻²⁴ Depending on the geometry of the probe and the mass flow of gas issuing from it, more or less severe concentration gradients occur at the tip of the probe and persist downstream for some distance before complete mixing occurs. It has been noted²⁴ that two opposing errors are introduced into observed rate measurements as a result of delayed mixing, one due to the reduced extent of reaction in regions where mixing has not occurred, the other to enhanced reaction along boundaries where high local concentrations of reactants exist. Since these effects do not in general cancel, precise analysis of the kinetic data requires prior careful analysis of the flow.²²⁻²⁴ An exception is the case where a difference technique (e.q. use of a movable probe) can be used to approximately cancel the effects of anomalous reaction in the vicinity of the tip.²¹ This was the type of method which was adopted in these studies.

A preliminary experiment was designed to examine the degree of mixing between probe gas and helium carrier gas as a function of distance downstream from the tip of the probe. PF₃ was introduced through the probe to give a pressure of ca. 300 mTorr in the reactor, corresponding to a flow of 0.79 Torr l./sec. The intensity of the m/e 69 ion peak from PF₃, which is a measure of the axial PF₃ concentration, was measured at various probe positions with respect to the end of the flow tube. Figure 2 is a plot of the log of the m/e 69 ion intensity at any probe position minus the position independent intensity achieved at large distances from the leak. The mixing is approximately exponential with a half-life of ca. 1 cm. The results were the same for lower flows of PF₃ (0.20 and 0.40 Torr l./sec).

Methods of calibration under various conditions of flow and temperature and the determination of the relative sensitivity of BH_8 have been described previously.

Materials. $BH_{3}PF_{3}$ was prepared according to the method of Parry and Bissot.²⁰ The material was distilled in the same manner as $BH_{3}CO$, the preparation of which is described elsewhere.²⁵ The maximum impurities after distillation were 5% of $B_{2}H_{6}$ or of PF_{8} .

 $BH_{\theta}NMe_{\theta}$ was prepared by reaction between diborane and trimethylamine. The 1.2 mmol of $B_{2}H_{\theta}$ and 3.5 mmol of $Me_{\theta}N$ were condensed at -196° into a U trap on a vacuum line and warmed slowly to -60° . Excess amine and other volatiles were distilled by several freeze-pump-thaw cycles between -60° and room temperature. The final vapor pressure of *ca*. 0.8 Torr at room temperature corresponds to that reported for the adduct.²⁶ A partial mass spectrum of this material was obtained and found to correspond within experimental precision to that of the product observed in the trimethylamine experiments. The relative intensities



Figure 2. Plot of the log of the m/e 69 ion signal from PF₃ at any probe position minus the intensity at long mixing times at 298°K, 4.6 Torr total pressure, and a partial pressure of PF₃ of 300 mTorr.

of ion peaks m/e 73:72:71 were as follows: prepared adduct, 5.3:100:31; observed product, 2.9:100:30.

 PF_3 of unspecified purity was obtained from Peninsular ChemResearch and trimethylamine of stated purity 99.0% from Matheson Co.

Results

 $BH_3 + PF_3 \xrightarrow{k_2} BH_3 PF_3$. The main kinetic data on this reaction are given in Table I. $T_{\rm R}$ is the mean temperature along the recombination zone and $T_{\rm D}$ the maximum temperature in the decomposition zone. t is the reaction time defined by l/v, where l is the length of, and v the temperature corrected²⁷ linear flow rate through, the recombination zone. p is the pressure read at the bottom of the flow tube after steady flow is established. The mass spectrometer sensitivity S is expressed in the same arbitrary units used previously.¹⁷ The measured pressures $(P)_0$, $(P)_s$, and $(P)_L$ are defined above. BH_3 pressures were measured with PF₃ present in the flow stream at the corresponding pressures $(PF_3)_0$. An exception to this procedure occurs in experiment 27 where all but one of the values for $(BH_8)_s$ were measured without PF₃ present and are indicated by parentheses. Adding PF₃ to the flow stream does not measurably change the BH₃ level, as indicated by the remaining value not in parentheses. However, a similar check at the long profile shows a decrease in BH₃

(27) The correction to the flow rate measured at room temperature is $T_{\rm R}/298.~$ See ref 24.

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Conditions	Expt	(PF₀)₀	(BH₅CO)¢	(BH₃CO)g	(BHs)g	(BH₃)L	(BH ₈)	(BH ₈ PF ₈)s	(BH₃PF₅)L	10-8 k ₂ , l./mol sec
$T_{\rm R} = 500^{\circ} {\rm K}$		(10.0	47.0	15 1	10.2	1.0	5.6		0.99	0 0
$T_{\rm D} = 0.00 {\rm K}$	24	10.0	21.0	10.1	7 1	1,0	4.0		0.22	15
$t = 0.537 \mathrm{msec}$		20.2	29.5		1.1	4.4 0.0 7	4.9		0.20	1.0
$10^{-8}v = 7.45 \text{ cm/sec}$		40.0	18.6		3,3	0.87	2.1		0.25	1.5
P = 5.74 Torr		(45.0)	47.9	15.1	10.2	0.66	5.4	<0.02	0.70	1.7
S = 13.6)										
$T_{\rm R} = 507^{\circ} {\rm K}$	30	(52.5)	14.7	5.0	2.1	1.8	2.0		0.18	1.1
$T_{\rm D} = 649^{\circ}{\rm K}$		52.5	33.2	11.2	7.6	3.2	5.4		0.37	0.80
t = 0.513 msec		52.5	60.2	22.0	8.5	6.0	7.2		0.49	0.79
$10^{-3}v = 7.80 \text{ cm/sec}$		126.2	14.7	5.0	1.7	1.5	1.6		0.31	0.92
P = 5.79 Torr		126.2	33.2	11.2	6.5	2.6	4.6		0.41	0.43
S = 18.2		126.2	60.2	22.0	6.9	5.1	6.0	<0.06	0.54	0.43
,		(12.7	11 0		(0.91)	0.00	0.45		0.086	7.5
		12.7	19.5	69	(1 8)	14	16		0 059	1.5
$T_{\rm R} = 494^{\circ} {\rm K}$		12.1	36.0	11 6	(1,0)	2.1	2 2		0.006	12
$T_{\rm D} = 652^{\circ}{\rm K}$		12.1	11 0	11.0	(1.0)	2.2	0.0		0.000	1.0
t = 0.611 msec		50.3	11.0		(0.91)	0.0	0.45		0.20	4.0
$10^{-8n} = 6.58 \text{ cm/sec}$	27	{ 50.3	19.5	6.9	(1.8)	1.2	1.5		0.35	2.4
P = 5.62 Torr		50.3	36.0	11.6	(4.3)	2.2	3.2		0.40	1.2
		136	11.0		(0.91)	0.04	0.48		0.43	3.3
o = 1(.8)		136	19.5	6.9	1.8	0.74	1.3		0.83	2.4
		136	36.0	11.6	(4.3)	1.7	3.0	<0.11	1.07	1.3

Table I: Partial Pressures of the Adduct from the Reaction of BH_s and PF_s in mTorr at 500°K and a Total Pressure of 5.7 Torr

from 1.3 to 0.74 mTorr upon adding 136 mTorr of PF₃. This corresponds to a second-order rate constant of 1.7 \times 10⁸ l./mol sec based on BH₃ loss.

 (\overline{BH}_3) is the arithmetic mean of $(BH_3)_S$ and $(BH_3)_L$. No measurable BH₃PF₃ was observed for the short profile within the indicated limits of detectability. The precision in measuring (BH_3) is low and stems from the fact that it is calculated from m/e 13 ion intensities corrected for large contributions from BH₃CO and smaller ones from B_2H_6 and BH_3PF_3 . The total correction varies between 40 and 80% of the observed (13⁺) intensity. The contributions to m/e 13 from these species are determined from the intensities of major ions (n^+) and the following ratios $(13^+/n^+): (13^+/40^+)$ - $BH_{3}CO = 0.28$, $(13^{+}/26^{+})B_{2}H_{6} = 0.12$ and $(13^{+}/26^{+})B_{2}H_{6} = 0.12$ 100^+)BH₃PF₃ = 0.31. The intensities of these major ions and of m/e 88 from PF₃ were used without correction to calculate the other pressures in Table I. The rate constants appearing in Table I were calculated from the approximate expression

$$k_2 = \frac{(\mathrm{BH}_3\mathrm{PF}_3)_{\mathrm{L}}}{(\mathrm{PF}_3)_0(\overline{\mathrm{BH}}_3)_0}$$

The average value for k_2 , weighted in a manner which is appropriate for data in which there is large scatter,²⁸ is 1.51×10^8 l./mol sec with an error factor (corresponding to one standard deviation) of 2.1. This value is the same as that calculated above on the basis of BH₃ loss.

A separate experiment was done to determine the extent of $BH_{3}PF_{3}$ decomposition in the reaction zone under the conditions used in the measurements of the association reaction. The decomposition was followed by observing the m/e 100 ion signal from BH₃PF₃ for various leak settings and reaction times at a uniform temperature of 494°K. This was accomplished by using three flat temperature profiles of lengths in the ratio 1:2:3 extending up to the sampling orifice. The two reaction times, 0.324 and 0.648 msec, were established by the displacements between the short profile and each of the two longer ones. Data obtained for two mass flows of BH₃PF₃ are plotted against reaction time in Figure 3. The first-order rate constant obtained from the averaged slopes is $ca. 300 \text{ sec}^{-1}$ at 494°K and 6.0 Torr of helium pressure. Calculations based on this value indicate a correction of no more than 10% to k_2 to account for decomposition of product. This correction was judged small enough to be negligible. The facts that the measurements of k_2 were made at the lowest possible reaction zone temperature and $BH_{\$}PF_{\$}$ appears partially decomposed at this temperature rule out the measurement of an activation energy for k_2 .

An additional set of experiments was designed to test whether the following reactions were contributing significantly to the formation of adduct observed.

$$PF_3 + BH_3CO \longrightarrow PF_3BH_3 + CO$$
 (a)

$$PF_3 + B_2H_6 \longrightarrow PF_3BH_3 + BH_3$$
 (b)

Procedures similar to those discussed above yielded the following upper limits to the respective bimolecular rate constants: $k_a \leq 4 \times 10^6 \text{ l./mol sec and } k_b \leq 1.1 \times 10^7$

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Figure 3. First-order plots for the loss of BH_3PF_3 as a function of time for two initial values of (BH_3PF_3) at 500°K and a total pressure of 6 Torr (*ca.* 98% helium).



Figure 4. Borane adduct observed as a function of initial PF_3 partial pressure from Table I. Triangles, squares, and circles refer to $(BH_3)_8 = 0.91$, 1.8, and 4.3 mTorr, respectively.

l./mol sec, both at 500°K and 6 Torr of helium pressure. Calculations based on these values indicate that as much as 10% of the adduct may be formed by reaction a and 1% by reaction b.

It has been assumed thus far that formation of BH_3 -PF₃ from BH_3 and PF₃ is first order in both reactants. First-order dependence on PF₃ is demonstrated in Figure 4, where product observed is plotted against PF₃ pressure at several fixed levels of BH_3 . Whereas these plots show good linearity, similar plots of product vs. BH_3 pressure show positive curvature and more scatter. The curvature arises from the approximate expression used to calculate the rate constant and the fact that this expression ignores the loss of BH_3 by the competitive recombination reaction to form diborane. Thus, the approximation of the average (BH_8) as the mean of the initial and final values overestimates the true average (BH_3) and the error increases for increasing initial (BH_3) and decreasing PF₃ pressures. The resulting negative error in the rate constant is not readily corrected. However, the error is small compared with the precision in measuring k_2 . As far as can be judged, the association reaction is first order in BH₃ as well as PF₃.

 $BH_3 + NMe_3 \xrightarrow{k_b} BH_3NMe_3$. The kinetics of this process were studied using BH_3PF_3 as the source of BH_3 . Trimethylamine was injected directly into the reaction zone through the inlet probe and the formation of BH₃-NMe₃ was observed as a function of probe position and mass flows. BH₃PF₃ decomposes completely in the decomposition zone to yield PF₃ and BH₃. The identification of the amine adduct by the mass spectrum of authentic material was discussed above. The data of kinetic value are given in Table II, where the reaction parameters have the same meaning as in Table I. The reaction time t, however, is now proportional to the distance, l, between tip of probe and end of flowtube. A long profile permitting a maximum reaction zone length of 4.20 cm was used to obtain all data except the BH₈ pressure. The latter was measured at the midpoint of the reaction zone by reproducing the same temperature profile 2.15 cm closer to the leak. This midpoint value, (BH3)m, was used to calculate the BH3 level along the entire recombination zone, in the absence of amine, using the previously reported decay of BH₃.¹⁷ These calculated values of the BH₃ level at each probe position are listed in Table II. They are denoted as $(BH_3)_0$ as they are the initial partial pressures of BH_3 at the indicated probe positions.

Adduct pressures observed for various times and reactant pressures are also listed in Table II. The

Table II: Partial Pressures of the Adduct from the Reaction of BH_{3} and $N(CH_{3})_{3}$ in mTorr at 500°K and a Total Pressure of 5.5 Torr

Conditions	(Me3N)	l. cm	NMes)	(BH ₈)0
$T_{\rm R} = 501^{\circ}{\rm K}$ $T_{\rm D} = 655^{\circ}{\rm K}$ $10^{-3}v = 7.92 \text{ cm/sec}$ P = 5.52 Torr	6.25	$\begin{cases} 0.00 \\ 1.05 \\ 2.05 \\ 3.20 \\ 4.20 \end{cases}$	$\begin{array}{c} 0.34 \\ 0.49 \\ 0.70 \\ 0.69 \\ 0.81 \end{array}$	2.78 3.00 3.24 3.67 4.27
S = 1.75 (BH ₃ PF ₈) ₀ = 27.8 mTorr (BH ₃) _m = 3.2 mTorr	16.4	$\begin{cases} 0.00 \\ 1.05 \\ 2.05 \\ 3.20 \\ 4.20 \end{cases}$	$0.65 \\ 0.89 \\ 1.15 \\ 1.38 \\ 1.58$	2.78 3.00 3.24 3.67 4.27
	51.4	$\begin{cases} 0.00 \\ 1.05 \\ 2.05 \\ 3.20 \\ 4.20 \end{cases}$	$0.99 \\ 1.50 \\ 1.80 \\ 2.59 \\ 2.82$	2.78 3.00 3.24 3.67 4.27



Figure 5. Trimethylamine borane adduct as a function of probe position for $(Me_8N)_0 = 16.4 \text{ mTorr}$ at 500°K and a total pressure of 5.5 Torr.

data for $(NMe_3)_0 = 16.4$ mTorr are illustrated graphically in Figure 5. A sizeable amount of adduct is observed even at the shortest probe position (l = 0.0cm), indicating that considerable reaction occurs in the vicinity of the probe tip. (The sampling leak is situated about 4 mm past the end of the flow tube.) Mixing effects are therefore significant and a simple calculation of the rate constant analogous to that used for the PF₃ studies is not applicable. A differential method was therefore used, employing the variation of adduct observed vs. probe position to extract the rate constant.

The differential rate equation for formation of adduct (A) can be written as

$$\frac{\mathrm{d}(\mathrm{A})}{\mathrm{d}t} = -\frac{\mathrm{d}(\mathrm{BH}_{\mathfrak{d}})}{\mathrm{d}t} = k_{\mathrm{t}}(\mathrm{Me}_{\mathfrak{d}}\mathrm{N})(\mathrm{BH}_{\mathfrak{d}}) \tag{1}$$

since in the presence of excess amine, adduct formation is the major pathway for loss of BH_3 . The integrated rate expression is

$$\log \frac{(BH_{3})_{0}}{(BH_{3})} = \log \frac{(BH_{3})_{0}}{(BH_{3})_{0} - (BH_{3}NMe_{3})} = \frac{(\overline{Me_{3}N})k_{t}t}{2.303} \quad (2)$$

if 1:1 stoichiometry between BH_3 lost and adduct formed and near constancy of the amine pressure are assumed. The error in neglecting BH_3 loss by dimerization is greatest at the lowest amine pressure. Here, for example, the error in log $(BH_3)_0/(BH_3)$ is about 30% at l = 2.0 cm and $(Me_3N)_0 = 6.25$ mTorr. A typical plot of log $(BH_3)_0/(BH_3)$ (as defined above) vs. probe position is shown in Figure 6 with the open circles. The pronounced curvature at longer reaction times (larger l) is partly attributable to the approximation discussed above, since the BH_3 concentration increases with distance from the end of the flow tube. It may also be due to a systematic error in the relative sensitivity of BH_3NMe_3 with respect to BH_3 that puts



Figure 6. Plot of log $(BH_{\mathfrak{s}})_0/(BH_{\mathfrak{s}})$ vs. probe position for $(\overline{Me_{\mathfrak{s}}N}) = 15.6$ mTorr where $(BH_{\mathfrak{s}}) = (BH_{\mathfrak{s}})_0 - (BH_{\mathfrak{s}}NMe_{\mathfrak{s}})$. The data is from Table II. The open and closed circles refer to unnormalized and normalized functions, respectively (see text).

an apparent upper limit on the fraction of BH_3 which reacts to give adduct. The nonzero intercept is largely due to excess reaction occurring in the vicinity of the probe tip, which inflates the ordinate function at shorter probe positions. To approximately correct for excess reaction at the tip, the data were replotted using the following modified rate equation

$$\log \frac{(BH_3)_0 - (BH_3NMe_3)_0}{(BH_3)} = \frac{(\overline{NMe_3})k_t t}{2.303}$$
(3)

where $(BH_3NMe_3)_0$ is the adduct pressure observed at l = 0.0 cm. This modification normalizes log (BH₃)₀/ (BH₃) to zero at zero probe position. The normalized plot is shown by the solid circles in Figure 6. The slightly greater slope of the linear portion of this curve is a better measure of the second-order rate constant k_2 than that of the original curve. According to eq 2 the slope of a plot such as that shown in Figure 6 divided by the average amine pressure yields k_t directly. The average amine pressure is approximately $(\overline{Me_3N}) =$ $(Me_3N)_0 - \frac{1}{2}(BH_3NMe_3)$, where the 1:1 stoichiometry between amine lost and adduct formed is used to account for the small depletion of amine during reaction. The best estimate of k_t , using all the data, is obtained by taking the slope of the plot shown in Figure 7, where the initial slopes of three curves such as that shown in Figure 6 are plotted against amine pressure. The secondorder rate constant obtained from the normalized data is $k_{\rm t} = 1.3 \times 10^9$ l./mol sec at 500°K and 5.5 Torr helium pressure.

It remains to examine possible corrections for alternate pathways for the formation or loss of adduct. At these temperatures and reaction times the decomposition of adduct is not likely to be significant. Although



Figure 7. Initial slope of $\log (BH_3)_0/(BH_3)$ vs. time plotted against amine pressure. Closed and open circles represent slopes of normalized and unnormalized curves, respectively (see Figure 6 and text).



Figure 8. Plot of log $(B_2H_6)_0/(B_2H_6)$ vs. probe position for $(Me_8N)_0 = 13.7$ mTorr where $(B_2H_6) = (B_2H_6)_0 - (BH_3NMe_3)$.

the decomposition of BH_3PF_3 was found to be appreciable, its dissociation enthalpy (ca. 23 kcal)²⁹ is considerably less than that estimated for BH_3NMe_3 (32 kcal).³⁰ The direct reaction between amine and BH_3PF_3 is excluded by the experimental method, but the following reaction can occur

$^{1}/_{2}B_{2}H_{6} + Me_{8}N = BH_{8}NMe_{8}$

since diborane is present in the reaction zone from the recombination of BH₃ (typically 3 mTorr at the midpoint of the reaction zone in the absence of amine). A control experiment to assess the importance of this process was performed. Diborane and amine were introduced into the reactor under conditions similar to the experiments with BH₃. An example of a plot of log $(B_2H_6)_0/[(B_2H_6)_0 - (BH_3NMe_3)]$ vs. probe position is given in Figure 8. The measured rate constant is 2.9 $\times 10^8$ l./mol sec and probably refers to the reaction

$$B_2H_6 + Me_3N \longrightarrow BH_3NMe_3 + BH_3$$

although the mechanisms suggested by Bauer' cannot be ruled out. It is not necessary to know the actual reaction, however, to correct k_t . Under the conditions used to measure the reaction of BH₃ with amine, the reaction of amine with diborane accounts for 15% of the total adduct observed and the final corrected value is $k_t = 1.1 \times 10^9 \, \text{l./mol sec}$ with an estimated error factor of 2 to 3.

Discussion

The rate constants measured in this work are compared with measurements on the reaction of BF₃ with $(CH_3)_3N$ in Table III. The reaction of BF₃ with PF₃ to form an adduct has not been observed. Although the rate constants for the reaction of BF₃ were measured at lower temperatures, the temperature dependence of this reaction is probably insignificant.¹⁰ As the species involved in these reactions are fairly small, one must consider the possibility that the rate constants measured are not the high-pressure limiting values. Unfortunately, the technique used in our study is poorly suited for total pressure variation and consequently we have no direct information on this point.

Table III: Rate Constants for the Formation of Donor-Acceptor Complexes								
$A + B \xrightarrow{k_{AB}} AB$								
A	В	kAB, l./mol sec	Ea, kcal	Pressure, Torr	Ref			
BH_{3}	PF_{3}	$1.5 imes10^{8}$ a		6	This work			
BH_3	$(CH_3)_3N$	$1.1 imes 10^9$		6	This work			
BF_3	$(CH_3)_3N$	$2.8 imes10^9$	$<\!\!3$	0.1	10			
BF_3	$(\mathbf{CH}_3)_3\mathbf{N}$	\geqslant 5 $ imes$ 10°		Variable	11			
^a Ma	y not be the	high-pressure	limiti	ng value.				

As was mentioned above, however, the ratio of rate constants for the reaction of monomethylamine and trimethylamine with BF₃ has been measured as a function of total pressure.¹¹ It appears clear from this work that the reaction of monomethylamine with BF₃ would be in the falloff region under our conditions. For this reason, it is quite possible that the reaction of BH₃ with PF₃ is also in the falloff region under our conditions. Because of this uncertainty, 1.5×10^8 l./mol sec must be taken as a lower limit for the rate constant. On the other hand, the rate constant for the reaction of trimethylamine with BF₃ under our conditions would probably be within a factor of 2 or 3 of the high-pressure limiting value. Therefore, our value for the reaction of

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(30) R. E. McCoy and S. H. Bauer, *ibid.*, 78, 2061 (1956).

BH₃ with trimethylamine is probably equal, within experimental error, to the high-pressure limiting value.

The comparison of the rates for the association of trimethylamine with BF₈ and with BH₈ is informative about the role of boranes as electron pair acceptors. Any ordering of so-called "acceptor strength" based on simple structural correlations is apt to be misleading. Although BH₈ is estimated to be much less stabilized in its planar geometry than BF_{3} ,^{8,9} it is clearly an even less efficient acceptor toward trimethylamine than BF₈. A similar conclusion can be made with respect to the reference base pyridine on the basis of thermochemical results.^{4,31} It is evident that the efficiency of BH₃ as an acceptor species in the presence of a typical amine donors is not enhanced by virtue of its more flexible structure compared with BF_3 . Apparently, in the reaction of BF₃ with amine donors, even as highly substituted as trimethylamine, any additional energy required to overcome planar stabilization in BF₈ is readily supplied by the reaction mechanism. This observation complies qualitatively with Mulliken's charge-transfer model if it is also postulated that a change from planar to pyramidal geometry is energetically favored during the approach of an electron to either BF_2 or BH_3 . Apparently this gain in energy is also sufficient to effect charge transfer at donor-acceptor separations large enough to make any difference in the relative sizes of BF_3 and BH_3 an unimportant factor in the reaction rates. Finally, as the intermolecular distance at which electron transfer takes place is reflected to some extent in the collision efficiency with which these reactions take place, our results indicate that the interaction distance for BF_3 is larger than for BH_3 . This in turn suggests a larger electron affinity for BF_3 than for BH_3 , which is quite reasonable.

Under our conditions, BH_3 reacts less efficiently with PF_3 than with $(CH_3)_3N$. However, if one were able to take into account the falloff behavior of the PF_3 system, the rate constants might well turn out to be comparable at the high-pressure limit.

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The Dynamic Adsorption of Water Vapor by a Fiber Drawn

from a Melt of Vycor

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The adsorption of water vapor was measured volumetrically on pristine nonporous fiber drawn from a melt of Vycor rods at 2050°. The fiber was pristine in that it had never been in contact with aqueous media or high relative humidities prior to the adsorption measurements. The krypton surface area of the fiber was 0.073 m^2/g . One sample of fiber was used for all reported measurements, and it was heated under vacuum to either 300, 500, or 800° before each exposure to water vapor. The water vapor adsorption was then followed at either 60, 80, 100, or 120° at p/p_0 of 0.04 and below, where p is pressure and p_0 is the vapor pressure of water at the temperature of adsorption. The amount of water vapor adsorbed increased with time, up to contact times of 4000 min. The hydration of a silica network, containing 3% boric oxide, was a dynamic process with a positive temperature coefficient over the experimental range employed. The data were fitted by an isochronal adsorption model where each isochrone followed a linear behavior $N_{t,T} = k_{t,T}p + i_{t,T}$, where $N_{t,T}$ is the amount adsorbed, $k_{i,T}$ the slope, and $i_{i,T}$ the intercept on the $N_{i,T}$ axis; the subscripts t and T designate the time and temperature, respectively. The significance of the constants $k_{i,T}$ and $i_{i,T}$ are discussed. Desorption measurements indicated that the water vapor was adsorbed tightly. The similarity of the results after fiber pretreatment at 300, 500, or 800° indicated that the interior of the fiber could be dehydrated with relatively little change in the surface sites. This was indicated by a similar magnitude in the interaction with water vapor measured at 120°. The first stage of the surface hydration process was the dissociative adsorption of a water molecule and the hydration of a siloxane bond. The second stage, in rapid succession, was the further adsorption of water molecules through hydrogen bonding to the surface products formed.

Introduction

The boundary of a glass fiber at the gas-solid interface can gain or lose water by (a) adsorption or desorption process *via* the gas phase and (b) migration from and to the bulk glass by some solid transport mechanism. At sufficiently high temperatures and partial pressures of water vapor, both processes can contribute and the overall gain or loss may be written