Table I. Values of van der Waals a and Molecular Polarizability, α, for Several Molecules and Thermodynamic Constants for Formation of Gas-Phase Complexes with I_2

Compound	Temp, °C	K_c,[a] l. mol^{-1}	$-\Delta E$,[a] kcal	Ref	a,[b] l.^{2} atm mol^{-1}	$\alpha \times 10^{25}$,[b] cm^3
Hexane	37	3.4		*c*	24.8	117.8
Benzene	35	4.2	1.4	*d*	18.7	103.2
	35	3.1	1.8	*e*		
Diethyl ether	35	4.4		*c*	17.4	87.3
	35	5.5	2.6	*d*		
	35		4.0	*f*		
	35	6	3	*g*		
Carbon dioxide	35	0.8	1.4	*h*	3.6	26.5

[a] For formation of the 1:1 complex between compound and I_2; extrapolated to temperature indicated if necessary. [b] As tabulated in J. R Partington, "An Advanced Treatise on Physical Chemistry," Longmans, Green and Co., London, 1954; Landolt-Bornstein, "Zahlenwerte und Functionen," Vol. I, Part 3, Springer-Verlag, Berlin, 1951, pp 510–512. [c] This work. [d] F. T. Lang and R. L. Strong, *J. Amer. Chem. Soc.*, **87**, 2345 (1965). [e] D. Atack and O. K. Rice, *J. Phys. Chem.*, **58**, 1017 (1954). [f] J. Grundnes and M. Tamres, in press. [g] Calculated from gas solubility data of W. Brüll and W. Ellerbrock, *Z. Anorg. Allg. Chem.*, **216**, 353 (1934). [h] Calculated from gas-phase solubility data of H. Braune and F. Strassman, *Z. Phys. Chem., Abt. A*, **143**, 225 (1929).

stabilize the 1:1 complexes, the order of K_c and $-\Delta E$ values should be hexane > benzene > diethyl ether > CO_2. Assuming that hexane–I_2 is stabilized solely by van der Waals forces, one may estimate that the stability of diethyl ether–I_2 owes roughly 50% to CT interaction and 50% to dispersion. The benzene–I_2 complex is probably stabilized less than 25% by CT forces. Although these conclusions are qualitative and tentative, they do lend support to recent arguments that values of ϵ for CT bands of gaseous complexes are lower than the corresponding condensed-phase values because of the variety of molecular arrangements which can contribute to the stability of the 1:1 complex.[18] Most of the molecular forms of weak gas-phase complexes presumably do not contribute significantly to the intensity of the CT band, whereas in the case of complexes in solution, the values determined for K_c and ϵ may pertain more nearly to oriented CT complexes.[18, 19]

Acknowledgment. Financial aid from National Science Foundation under Grants No. GP-8029 and GP-23278 is greatly appreciated.

(18) O. K. Rice, *Int. J. Quantum Chem., Suppl.*, **2**, 219 (1968).

(19) However, there is still considerable discussion regarding the interpretation and validity of values of K_c and ϵ for weak CT complexes in solution; see, for example, ref 2b and 3 and R. L. Scott and D. V. Fenby, *Annu. Rev. Phys. Chem.*, **20**, 125 (1969).

Reactions of Borane. II.[1] Absolute Rate of the Reaction of Borane with Ethylene in the Gas Phase

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Abstract: The reaction of borane (BH_3) with ethylene (C_2H_4) to produce ethylborane ($C_2H_5BH_2$) as a primary product has been shown to occur in the gas phase. At 450° and 4.7 Torr total pressure of helium, the absolute bimolecular rate constant for this reaction is given by the expression $\log k_1 = 10.2 - (2{,}000/4.575T)$ l. mol^{-1} sec^{-1}. Estimates of the rate constants for the self-association and hydroboration of ethylborane are also presented. The significance of these results with respect to the reactivity of borane and the nature of the hydroboration reaction are discussed in terms of the absolute rate theory.

We have recently reported measurements on the rate of the self-association reaction of borane, BH_3, to form diborane, B_2H_6.[1] This reaction is one of the characteristic reactions of the borane molecule, and these measurements have illustrated one aspect of the reactivity of this unstable species. In an attempt to further our understanding of the reactivity of a species possessing a free valence orbital, we have now both qualitatively and quantitatively examined the reaction of free borane with ethylene. This reaction is the prototype of the hydroboration reaction—a reaction which has been studied extensively in the liquid phase and in solvent systems.[2] In these studies, it is diborane or a borane–solvent adduct and the olefin which are the initial reactants. A few gas-phase studies have been reported,[3–5] and here, too, diborane is the initial reactant. Of course this does not necessarily mean that the olefin reacts directly with either diborane or the borane–solvent adduct, as it is possible that free borane is an active intermediate. In order

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(1) Part I: G. W. Mappes, S. A. Fridmann, and T. P. Fehlner, *J. Phys. Chem.*, **74**, 3307 (1970).

(2) H. C. Brown, "Hydroboration," W. A. Benjamin, New York, N. Y., 1962.

(3) D. T. Hurd, *J. Amer. Chem. Soc.*, **70**, 2053 (1948).

(4) A. T. Whatley and R. N. Pease, *ibid.*, **76**, 835 (1954).

(5) H. H. Lindner and T. Onak, *ibid.*, **88**, 1886 (1966).

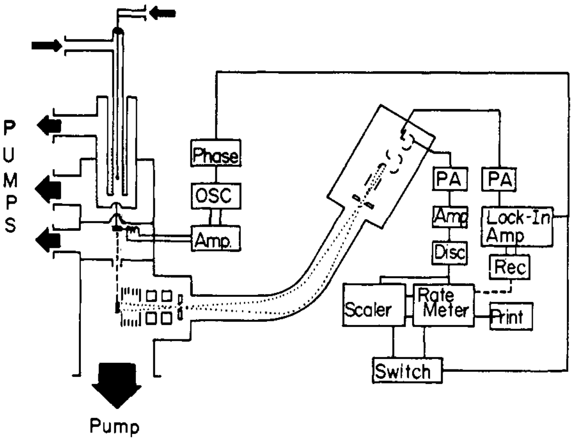

Figure 1. Schematic drawing of the present experimental apparatus.

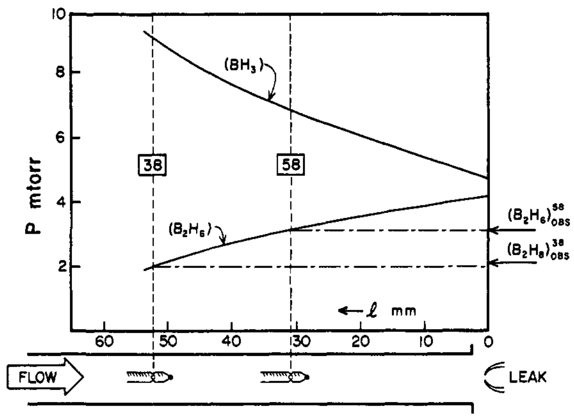

Figure 2. Schematic drawing of the flow reactor showing the concentration profiles of BH_3 and B_2H_6 in the absence of C_2H_4. The observed levels of B_2H_6 in the presence of C_2H_4 for the two indicated probe positions are shown at the right of the figure.

to examine the role of BH_3 in the hydroboration reaction and to characterize another aspect of the reactivity of BH_3, we have directly examined the simple reaction

$$BH_3 + C_2H_4 \longrightarrow C_2H_5BH_2$$

in the gas phase.

Experimental Section

Materials. Borane was produced as described in detail previously.[1,6] However, BH_3PF_3 was used as a source of BH_3 rather than BH_3CO. It was found that the former produced BH_3 at lower decomposition temperatures and thus in somewhat higher yields. As will be pointed out below, the characteristics of BH_3 produced from BH_3PF_3 are identical with those of BH_3 produced from BH_3CO. BH_3PF_3 was prepared by the method of Parry and Bissot[7] and was purified by trap-to-trap fractionation. The major impurities were PF_3 and B_2H_6 present at levels of less than 5 mol %. Diborane was prepared by the method of Jeffers[8] and was also purified by trap-to-trap fractionation. Ethylene (CP, Matheson) was used without further purification.

Flow Reactor. The flow reactor and the general reaction conditions used in these studies have been described in detail in two previous publications.[1,6] The reactor is schematically indicated in Figure 1. One modification was made, however. The previously solid thermocouple probe was replaced by a 2-mm i.d., 3-mm o.d. quartz tube. This tube, with appropriate flexible connections, allowed the introduction of a gas into the main flow at any desired position along the axis of the reactor through three equispaced 1-mm holes in the walls of the tube. A thermocouple is sealed in the end of the tube, and thus the tube continues to carry out the function of the thermocouple probe described previously. A sketch of the end of the modified probe is shown at the bottom of Figure 2. This modification was required to study the reaction of any species that would be likely to react with BH_3PF_3 in the high-temperature BH_3 preparation zone. It introduces a complication into the quantitative studies as one now has to worry about the time required for mixing. The probe is movable, however, and differential measurements are possible.

In these experiments a single temperature profile similar to that shown at the top of Figure 1 in ref 1 with a decomposition zone temperature of 635°K was used in each rate constant measurement. Measurements involved only changing the position of the gas probe and, consequently, the orifice temperature remained constant. Most of the measurements were made at a mean reaction zone temperature of *ca.* 440°K. Under these conditions, the temperature at the upstream end of the reaction zone was *ca.* 465°. The reaction zone consists of the zone in Figure 2 defined by l = 0–20 mm. In this study the diluent carrier gas was helium at a partial pressure in the reactor in the range of 4.7 Torr. Flow velocities range from 5 to 10 × 10^3 cm/sec and reaction times range from 1 to 5 × 10^{-4} sec. Calibrations were carried out as discussed previously.[1]

Analysis. The composition of the gas exiting from the reactor was determined by sampling with a small thin-edged orifice into a mass spectrometer system utilizing modulated molecular beam sampling. The complete system is shown schematically in Figure 1. The efflux of the sampling orifice is collimated into a molecular beam using a three-stage differentially pumped system. The molecular beam is crossed with an electron beam 13 cm from the sampling orifice, and resulting ions are accelerated, mass analyzed, and detected. The molecular beam is mechanically modulated at 160 Hz, and the signal from the electron multiplier is fed either to a narrow-band amplifier which is locked into the frequency and phase of the modulation device or to a modulated counting system. The latter system is new on our instrument and is similar in principle to others.[9] However, with the exception of the switch, it is constructed entirely of standard commercial (Ortec) components. The switch is a special discriminator that provides the gate signals for the two counters that are synchronized with the reference sine wave. An integral part of the system is a phase shifter (Ad-Yu Type 208) with a precision of 0.05°. It was recognized quite early in the development of the modulated molecular beam sampling technique that this technique not only discriminates against extraneous background ion signals but also provides a convenient means for the identification of the neutral species in the molecular beam.[9–11] The phase shift between the reference signal and the ion signal is related to the average flight time of the neutral molecule in the molecular beam that gives rise to the ion signal. Our technique[12] is to measure under operating conditions the apparent relative phases of two ion signals from different known unique molecular progenitors. With these two calibrations, the relative phase of any other ion signal yields an apparent molecular mass according to

$$m_x = \{[Sm_a^{1/2} - (\phi_a - \phi_x)]/S\}^2$$

where $S = (\phi_a - \phi_b)/(m_a^{1/2} - m_b^{1/2})$ and where ϕ_x is the relative phase of ion x, m_x is the apparent molecular weight of x, a and b refer to the two calibrating species, and the phase shifts due to differences in ion flight times have been neglected, as the correction involved is only 2%. For these experiments the average value of S is 0.91. As the relationship between the signal intensity and phase angle is essentially sinusoidal,[10,11] it is convenient to measure the phase angle at zero intensity. A typical measurement of the apparent phase of the m/e 41 ion signal is shown in Figure 3. The mass resolution is not very good, as the present experimental arrangement is a compromise between useful phase measurements and good signal-to-noise ratios. However, with the counting sys-

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(6) G. W. Mappes and T. P. Fehlner, *J. Amer. Chem. Soc.*, **92**, 1562 (1970).

(7) R. W. Parry and T. C. Bissot, *ibid.*, **78**, 1524 (1956).

(8) W. Jeffers, *Chem. Ind.* (*London*), 431 (1961).

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(12) T. P. Fehlner, *J. Amer. Chem. Soc.*, 90, 4817 (1968).

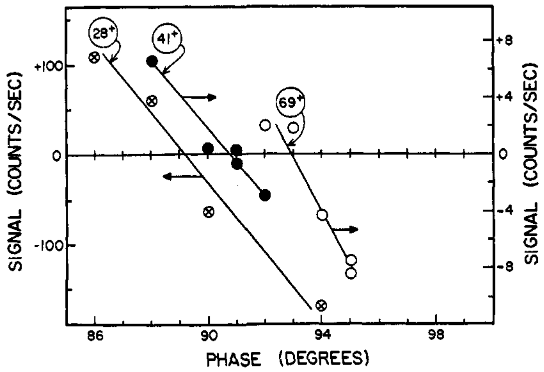

Figure 3. Determination of the relative phase of the *m/e* 41 ion signal produced from the reaction of BH_3 with C_2H_4. *m/e* 28 is derived from C_2H_4 and *m/e* 69 is derived from PF_3. Counting times of 100 sec were used.

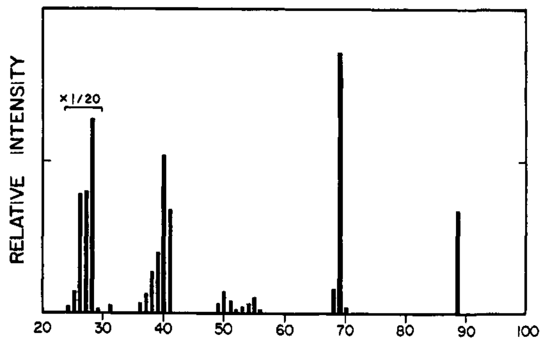

Figure 4. Mass spectrum of the products of the reaction of C_2H_4 with BH_3. $(C_2H_4)_0$ = 150 mTorr. $(BH_3)_0^{38}$ = 2 mTorr. The mean temperature was 445°K, while the total pressure was 4.7 Torr. The probe was at position 38 (see Figure 2), the flow velocity was 1.1×10^4 cm/sec, and the reaction time was *ca.* 5×10^{-4} sec.

tem described above, it is now possible to obtain valuable information on the molecular progenitors of low-intensity ions and consequently it is possible to identify reaction products present at low concentrations in the reactor.

Results

Identification of Products. The reaction products were identified by their mass spectra, by the relative phase of selected ion signals, and by the variation in selected ion intensities with reactant concentration changes in the reactor. However, before products of the reaction of C_2H_4 with BH_3 were investigated, some additional experiments were carried out to further confirm the presence of relatively high concentrations of BH_3 in our system. As was mentioned in the Experimental Section, BH_3PF_3 was used as a source of BH_3 in these experiments. Table I shows that the spectrum of BH_3 is independent of the nature of the source gas. The sensitivity of BH_3 calculated as noted in ref 6 was equal within experimental error to that calculated using BH_3CO as a source gas. In addition, the second-order rate constant for the association of BH_3 measured using BH_3PF_3 as a source gas was equal within experimental error to that reported previously using BH_3CO as a source gas.[1] Finally, Table II presents the results of the measurement of the apparent molecular weight of the neutral progenitor of the *m/e* 13 ion signal after passing BH_3PF_3 through the preparation zone described above. It is clear from the result that BH_3 is present. As B_2H_6 contributes to the *m/e* 13 ion signal, the measured apparent molecular weight of 14.3 indicates that BH_3 is present at higher levels than diborane. Indeed, one may calculate, with considerable uncertainty, that the ratio of BH_3 to B_2H_6 here is *ca.* 20.[11] This is consistent with the ratio reported previously.[6]

Table I. Mass Spectrum of Borane at 70 eV

Ion	Intensity	
	From BH_3CO[a]	From BH_3PF_3[b]
BH_3^+	30	29
BH_2^+	100	100
BH^+	18	21
B^+	8	7

[a] Reference 6. [b] This work.

Table II. Identification of BH_3 by Phase Measurements

m/e	ϕ, deg	Apparent mol wt	Neutral progenitor
69^+	12.4	88.0 (known)	PF_3 (known)
28^+	6.8	27.6 (known)	B_2H_6 (known)
13^+	4.8	14.3	BH_3

For the initial investigation of the reaction of BH_3 with C_2H_4, the partial pressure of BH_3 at position 38 in Figure 2 (l = 52 mm) was *ca.* 2 mTorr, while the partial pressure of C_2H_4 was *ca.* 150 mTorr. The total reaction time was *ca.* 5×10^{-4} sec and the total pressure was 4.7 Torr. Figure 4 presents a typical mass spectrum of the species effusing from the reactor under these conditions. The characteristic spectra of C_2H_4 and PF_3 are easily spotted. Small amounts of B_2H_6 and BH_3PF_3 are indicated by the presence of low-intensity *m/e* 22 and 23 ion signals and low-intensity *m/e* 99–102 ion signals, respectively (not shown in Figure 4). Easily measureable ion signals appear in the *m/e* 40 region, *m/e* 50 region, and at *m/e* 68 and 70. In addition, a small but significant ion intensity is measured at *m/e* 83. All of these last mentioned ion intensities depended on the presence of both BH_3 and C_2H_4. Consequently, these ions result from the interaction of BH_3 and C_2H_4. Simple consideration of the ions observed indicates that some or all of the following are possible products: ethylborane, $C_2H_5BH_2$; diethylborane, $(C_2H_5)_2BH$; triethylborane, $(C_2H_5)_3B$; ethyldiborane, $C_2H_5B_2H_5$; *sym*-diethyldiborane $[C_2H_5BH_2]_2$; and *asym*-diethyldiborane, $(C_2H_5)_2B_2H_4$. Ions were carefully sought at *m/e* 98, but none were observed. The presence of triethylborane is ruled out by this and by the phase measurements discussed below. The rest of the possible products cannot be immediately ruled out. Indeed, the large *m/e* 41 ion intensity need not indicate the presence of ethylborane, as both triethylborane and diethyldiborane (and therefore probably the others) have intense fragment ions at this *m/e* ratio.[13] Further information is required and is provided by the phase measurements described next.

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(13) I. Shapiro, C. O. Wilson, J. F. Ditter, and W. J. Lehmann, *Advan. Chem. Ser.*, No. 32, 127 (1961).

The relative phases (ϕ) of the *m/e* 68, 54, and 41 ion signals were measured as indicated above. For calibration the relative phase of the *m/e* 69 ion signal with only BH_3PF_3 in the flow stream and the relative phase of the *m/e* 28 ion signal with only C_2H_4 in the flow stream were measured. The former ion is due only to PF_3[14] while the latter is due to C_2H_4. An example of one of these measurements for *m/e* 41 is shown in Figure 3. All of these measurements were carried out at ethylene to borane ratios of *ca.* 15. The results of a single measurement are given at the left of Table III, while the average values are given in the fourth column. The number of measurements is indicated by the number in parentheses, and the uncertainty is estimated from the noise in the signals. It is certainly clear that the ion signal at *m/e* 41 is due mainly to ethylborane and that ethylborane is the primary product of the reaction of BH_3 and C_2H_4.[15] The apparent mass of the *m/e* 54 ion signal and the presence of a detectable *m/e* 83 ion signal indicate that these ions arise from diethyldiborane. The apparent absence of ethyldiborane (*m/e* 54 also) at high ethylene levels indicates that BH_3 is almost totally scavenged by ethylene. This is confirmed by the mass-balance experiments discussed below and, consequently, the diethyldiborane is probably the symmetrical species. Finally, the signals appearing at *m/e* 68 and 70 are due to diethylborane. Both the *sym*-diethyldiborane and diethylborane are secondary products resulting respectively from the self-association of ethylborane and the association of ethylborane with ethylene.

Table III. Identification of Products of the Addition Reaction by Phase Measurements

m/e	ϕ, deg	Apparent mol wt This work	 Av values	Neutral progenitor
69^+	92.9	88.0 (known)		PF_3 (known)
68^+	92.1	72	72 ± 15 (1)	$BH(C_2H_5)_2$
54^+	93.8	97	85 ± 20 (2)	$[BH_2(C_2H_5)]_2$
41^+	90.7	48	49 ± 8 (3)	$BH_2(C_2H_5)$
28^+	89.2	28.0 (known)		C_2H_4 (known)

Additional confirmation of some of these assignments was obtained by examining the variation in these ion signals with change in reactant concentrations. The best example of this type of experiment is shown in Figure 5. Although the slopes of these plots are not meaningful, it is quite clear that the species giving rise to the *m/e* 68 ion signal depends much more strongly on the partial pressure of ethylene than does the species giving rise to the *m/e* 41 ion signal. This is consistent with the assignment of *m/e* 68 as being due to diethylborane and *m/e* 41 as being due to ethylborane. This also means that at lower C_2H_4 concentrations the product diethylborane will diminish in importance. The other possible variations were examined, but these yield no obvious positive result. They were not, however, inconsistent with the above assignments.

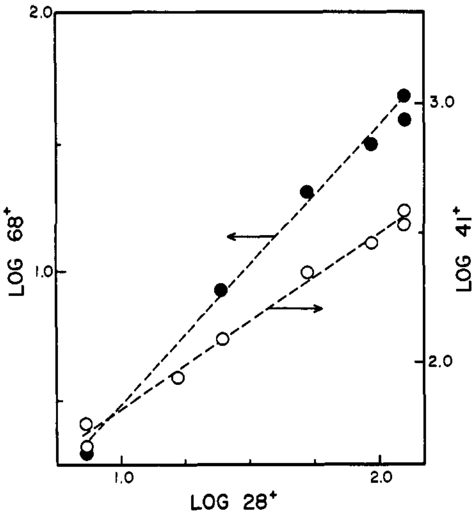

Figure 5. Variation in the *m/e* 68 and *m/e* 41 ion intensities with the partial pressure of C_2H_4 as represented by the *m/e* 28 ion signal. With the exception of $(C_2H_4)_0$, which was variable, the conditions of the experiment were similar to those of Figure 4.

Two control experiments were carried out to investigate the possibility that the products observed above could be the result of the direct reaction of C_2H_4 with BH_3PF_3 or B_2H_6. None of these products was observed, however, when using similar partial pressures of C_2H_4 and partial pressures of B_2H_6 and BH_3PF_3 at least ten times higher than that of BH_3 in the BH_3–C_2H_4 reaction system. These experiments allow an upper limit to be placed on the rate constant for the reaction of B_2H_6 with C_2H_4 of $k \leq 2 \times 10^6$ l. mol^{-1} sec^{-1} over the temperature of 300–600°K.

To summarize, the following reactions can take place in the reaction zone

$$BH_3 + C_2H_4 \longrightarrow BH_2(C_2H_5) \qquad (1)$$

$$2BH_2(C_2H_5) \longrightarrow [BH_2(C_2H_5)]_2 \qquad (2)$$

$$BH_2(C_2H_5) + C_2H_4 \longrightarrow BH(C_2H_5)_2 \qquad (3)$$

$$BH_2(C_2H_5) + BH_3 \longrightarrow B_2H_5(C_2H_5) \qquad (4)$$

$$2BH_3 \longrightarrow B_2H_6 \qquad (5)$$

Reaction 1 is the major process, as both $[BH_2(C_2H_5)]_2$ and $BH(C_2H_5)_2$ are minor products. At high C_2H_4 partial pressures, the RBH_2/BH_3 ratio is large and thus, under these conditions, processes 4 and 5 occur to only a minor extent. This point will be more firmly established in the next section.

Mass Balances and Sensitivities. The existence of the reaction of BH_3 with C_2H_4 to form the previously unknown species $C_2H_5BH_2$ has been established above. In order to measure the rate constant for this reaction, it is necessary to follow either the loss of BH_3 or C_2H_4 or the formation of $C_2H_5BH_2$. The first was not possible owing to the interference of ions from C_2H_4 with the strongest ion signals from BH_3. The second was possible but involved the measurement of small changes in a large and fairly noisy ion signal. The last was the best possibility but required the determination of a relative sensitivity for $C_2H_5BH_2$. Two approaches were used. The first involved the use of mass balances and the relative phase of the *m/e* 41 ion signal and yielded sensitivities for $C_2H_5BH_2$, $[C_2H_5BH_2]_2$, and $(C_2H_5)_2BH$. The second is based on the observation that one can effectively titrate all of the initial BH_3 with C_2H_4. This yielded a sensitivity for $C_2H_5BH_2$. A description of these approaches follows.

[14] The BH_3PF_3 is *ca.* 99% decomposed.

[15] For example, if one assumes that the only two species present are ethylborane and diethylborane, the measured phase would indicate an ethylborane to diethylborane ratio of 3.

Table IV. Partial Pressures (mTorr) of Products for Two Probe Positions

	Probe 38.0				Probe 58.0			
$(C_2H_4)_0$	$(BH_3)_0$	$(C_2H_5BH_2)$	$([C_2H_5BH_2]_2)$	$([C_2H_5]_2BH)$	$(BH_3)_0$	$(C_2H_5BH_2)$	$([C_2H_5BH_2]_2)$	$([C_2H_5]_2BH)$
				A[a]				
6.7	9.1	1.9	0.24	0.0	6.8	0.49	0.0	0.0
15	9.1	4.2	0.62	0.0	6.8	2.0	0.22	0.0
45	9.1	6.7	0.95	0.24	6.8	2.6	0.41	0.14
152	9.1	7.9	1.2	0.76	6.8	2.4	0.37	0.42
220	9.1	5.4	1.0	1.2	6.8	2.6	0.30	0.50
220	3.1	2.1	0.43	0.42	2.6	0.78	0.15	0.14
220	6.1	5.0	0.62	0.73	5.0	1.6	0.30	0.31
220	9.1	7.4	1.4	1.2	6.8	2.6	0.45	0.52
220	14.7	10.5	1.9	2.3	10.2	3.3	0.67	0.71
				B[b]				
9.3	1.9	0.11			1.4	0.13		
20	1.9	0.44			1.4	0.28		
45	1.9	1.0			1.4	0.38		
95	1.9	1.4			1.4	0.41		
145	1.9	1.6			1.4	0.45		

[a] $t_r = 2.06 \times 10^{-4}$ sec, $T_r = 430$°K. [b] $t_r = 1.70 \times 10^{-4}$ sec, $T_r = 445$°K.

The first method resulted from some observations of the behavior of the partial pressure of B_2H_6 in the presence of C_2H_4. The partial pressure of B_2H_6 observed at the sampling orifice decreased on the addition of C_2H_4 to the flow stream. This decrease is not due to the reaction of B_2H_6 with C_2H_4 as shown above, but rather to the opening of an additional reaction channel for BH_3. The interpretation of the decreases observed is most easily understood by considering Figure 2. The solid curves in the graph at the top of the figure denote the partial pressures of BH_3 and B_2H_6 in the *absence* of C_2H_4. These curves were constructed from spot measurements made in this study along with the more extensive measurements reported previously.[1] The two probe positions are indicated by 38 and 58 at 52 and 31 mm from the sampling orifice, respectively. The value of the partial pressure of B_2H_6 at position 38 is a minimum value for the B_2H_6 partial pressure at the sampling orifice in the presence of C_2H_4. In other words, if all of the BH_3 is scavenged by C_2H_4 added at position 38, the partial pressure of B_2H_6 measured at the sampling orifice would be 2 mTorr. The same holds true for position 58, except that here the minimum value is 3.1 mTorr. The observed values of B_2H_6 in the presence of a large excess of C_2H_4 (C_2H_4/BH_3 = *ca.* 20) are indicated by the arrows at the right of the figure. These measurements were made using the *m/e* 23 ion signal as a measure of B_2H_6. Under these conditions, it is clear that nearly all of the BH_3 is scavenged. Consequently, the following mass-balance equations may be written for a single probe position at high C_2H_4 partial pressures.

$$(C_2H_4)_0 - (C_2H_4) = (C_2H_5BH_2) + 2([C_2H_5]_2BH) + 2([C_2H_5BH_2]_2)$$

$$(BH_3)_0 = (C_2H_5BH_2) + ([C_2H_5]_2BH) + 2([C_2H_5BH_2]_2)$$

where (X) refers to the partial pressure of X, $(C_2H_4)_0$ refers to the partial pressure of C_2H_4 in the absence of BH_3, (C_2H_4) refers to the partial pressure of C_2H_4 in the presence of BH_3, and $(BH_3)_0$ is the BH_3 partial pressure at the injection position in the absence of C_2H_4. In addition, an equation relating the measured phase of the *m/e* 41 ion signal to the partial pressures of the various species contributing to this signal may be written as

$$\begin{aligned}(C_2H_5BH_2)\{S[(41.9)^{1/2} - (88.0)^{1/2}] + \phi_{41}\} &+ \\ ([C_2H_5BH_2]_2)\{S[(83.8)^{1/2} - (88.0)^{1/2}] + \phi_{41}\} &+ \\ ([C_2H_5]_2BH)\{S[(70.0)^{1/2} - (88.0)^{1/2}] + \phi_{41}\} &= 0\end{aligned}$$

where *S* has been defined above and ϕ_{41} refers to the difference between the relative phase of *m/e* 69 ion signal (from PF_3) and the relative phase of the *m/e* 41 ion signal. For a given set of conditions, these three equations may be solved to yield the partial pressures of the three species. It is not feasible to carry out this procedure over all the conditions desired; therefore, these partial pressures were converted into sensitivities (unit ion intensity per unit pressure) using the measured ion intensities of the *m/e* 41, 54, and 68 peaks. This assumes that the ion intensities are due only to one species, an assumption that is not true for the *m/e* 41 peak. On the other hand, as $C_2H_5BH_2$ is the major species present under all conditions, it is probably true that the majority of the *m/e* 41 ion signal is due to this species. As the pertinent fragmentation patterns are not known, this point cannot be proved. The sensitivities obtained by this method are: $S_{C_2H_5BH_2}$ = 42, $S_{]C_2H_5BH_2]_2}$ = 21, and $S_{[C_2H_5]_2BH}$ = 33 units/mTorr. Because of the uncertainties in the phase measurements, the last two sensitivities must be considered as estimates only.

The second method also makes use of the fact that the BH_3 can be effectively scavenged by C_2H_4. In this method the *m/e* 41 ion intensity is extrapolated to $1/(C_2H_4) = 0$. The extrapolated ion intensity and the initial BH_3 partial pressure at the probe position yield a sensitivity for $C_2H_5BH_2$. The average value obtained is 38 units/mTorr. The good agreement between the two methods does not alleviate the problem of the contribution to the *m/e* 41 ion intensity by the other species.

Rate Constants. The best data of kinetic value are given in Table IV. The ion intensities measured at the two probe positions were converted into partial pressures using the sensitivities derived above. As $C_2H_5BH_2$ is the primary and predominant product,

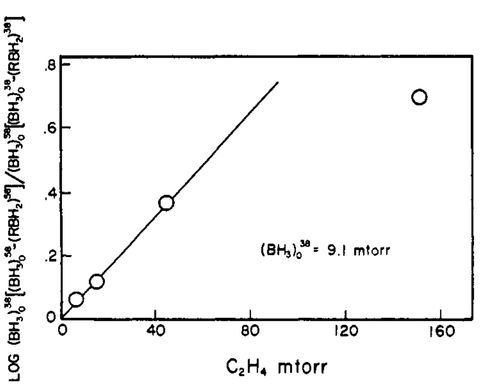

Figure 6. A plot of log $(BH_3)_0{}^{38}[(BH_3)_0{}^{58} - (C_2H_5BH_2)^{58}]/(BH_3)_0{}^{58}[(BH_3)_0{}^{38} - (C_2H_5BH_2)^{38}]$ *vs.* $(C_2H_4)_0$ for a $(BH_3)_0{}^{38}$ = 9.1 mTorr, a mean temperature of 430°K, and a total pressure of 4.7 Torr.

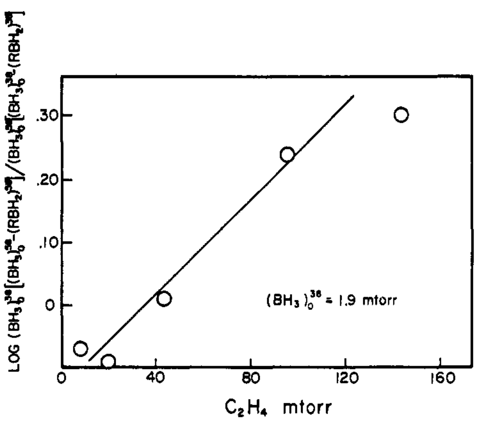

Figure 7. A plot of log $(BH_3)_0{}^{38}[(BH_3)_0{}^{58} - (C_2H_5BH_2)^{58}]/(BH_3)_0{}^{58}\cdot[(BH_3)_0{}^{38} - (C_2H_5BH_2)^{38}]$ *vs.* $(C_2H_4)_0$ for a $(BH_3)_0{}^{38}$ = 1.9 mTorr, a mean temperature of 445°K, and a total pressure of 4.8 Torr.

the rate constant for reaction 1 is calculated as if it were the exclusive reaction occurring in the reaction zone (l = 0–20 mm in Figure 2). In addition, most of the data were obtained when the ratio $(C_2H_4)/(BH_3) > 1$. Thus the integrated rate equation at any probe position is

$$\log [1 - (C_2H_5BH_2)/(BH_3)_0] = -k_1(C_2H_4)_0t/2.303$$

For any two probe positions two integrated equations may be combined to yield

$$\log (BH_3)_0{}^a[(BH_3)_0{}^b - (C_2H_5BH_2)^b]/(BH_3)_0{}^b[(BH_3)_0{}^a - (C_2H_5BH_2)^a] = k_1(C_2H_4)_0t_r/2.303$$

where t_r is the reaction time given in Table IV and a and b refer to the different probe positions. Figures 6 and 7 show the left-hand side of the last equation plotted *vs.* the partial pressure of C_2H_4 for two different initial BH_3 levels. These plots should be straight lines with a zero intercept and a slope of $k_1t_r/2.303$. The best curve through these points falls off at high C_2H_4 pressures. This is particularly evident for the higher partial pressure of BH_3 (Figure 6). This falloff is undoubtedly caused by the formation of diethylborane and diethyldiborane at the higher partial pressures. The best rate constant is taken as the initial slope and is indicated by the straight lines in the figures. The negative intercept in Figure 7 is probably caused by a systematic error in measuring the concentrations at the two probe positions. The rate constants obtained from Figures 6 and 7 are 2.5 × 10^9 and 1.4 × 10^9 l. mol^{-1} sec^{-1}, respectively. Within experimental error they are independent of the BH_3 partial pressure.

In order to investigate the temperature dependence of the rate constant, an experiment was carried out at a constant high value of C_2H_4 and three different reaction zone temperatures. The rate constants were calculated using the last equation given above, and the results are given in Table V along with the values calculated from Figures 6 and 7. The two values at 445°K should not be directly compared, as one is calculated on the basis of a single high value of C_2H_4. An Arrhenius plot of the last three values in Table V yields an activation energy of 2 kcal/mol with an uncertainty of 3 kcal/mol (see below).

The data in Table IV also provide estimates for the rate constants of reactions 2 and 3, the dimerization of ethylborane and the hydroboration of ethylborane, respectively. These rate constants were calculated from the approximate equations

$$k_2 = \Delta([C_2H_5BH_2]_2)/(\overline{C_2H_5BH_2})^2t_r$$

$$k_3 = \Delta([C_2H_5]_2BH)/(C_2H_4)_0(\overline{C_2H_5BH_2})t_r$$

where $\Delta(X)$ is the change in the partial pressure of X between the two probe positions and $(\overline{X})$ is the average partial pressure of X between the two positions. The average value of k_2 calculated in this fashion is 4 × 10^9 l. mol^{-1} sec^{-1}, while the average value of k_3 is 1 × 10^8 l. mol^{-1} sec^{-1}. The average deviation in both cases is *ca.* 30%. Reaction 2 appears to have no activation energy, while reaction 3 has an apparent positive activation energy.

Table V. Rate Constants for the Association of BH_3 with C_2H_4

$k_1 \times 10^{-9}$, l. mol^{-1} sec^{-1}	Mean temp, °K	$(BH_3)_0{}^{38}$, mTorr	$(C_2H_4)_0$, mTorr
2.5	430	9.1	Variable[a]
1.4	445	1.9	Variable[b]
0.9	445	2.0	130
1.4	530	2.0	130
1.6	590	2.0	130

[a] Figure 6. [b] Figure 7.

A number of errors in time, temperature, and analysis possibly present in these experiments have been discussed in the previous paper.[1] Some of these are modified by the changes in procedure noted in the Experimental Section. However, there is a substantial source of error associated with the introduction of a reactant through the probe (also described above). The biggest problem is associated with the mixing of the reagent in the flow stream. This causes errors both in time and effective concentration. As these data do not warrant the complex corrections described by others,[16] a simple differential technique was used to empirically remove the major mixing error. By injecting a stable gas (*ca.* 300 mTorr) into the flow stream and measuring the ion intensity *vs.* probe position, it was shown that mixing is approximately exponential, with a half-

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(16) E. E. Ferguson, F. C. Fehsenfeld, and A. L. Schmeltekopf, *Advan. At. Mol. Phys.*, **5**, 1 (1969).

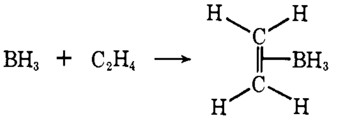
life of *ca.* 1 cm.[17] Consequently, the difference in measurements carried out at probe positions such as those indicated in Figure 2 yields changes due to reaction in the region where mixing is complete. For example, measurements made at positions 38 and 58 in Figure 2 constitute measurements in the zone defined by l = 0 to 20 mm.

The second problem, and also a large source of uncertainty, is the difficulty in obtaining a satisfactory sensitivity for ethylborane owing to the lack of information on the fragmentation pattern of diethyldiborane and diethylborane. Little can be done about this uncertainty. Finally, it has been assumed that ethylborane is stable at the reaction zone temperatures and times. This is a reasonable assumption, as borane is stable under these conditions.

To summarize, the quantitative measurements of the absolute rate constant k_1 are probably not better than a factor of 2 or 3. The uncertainty in the activation energy, E_1, is estimated to be 3 kcal/mol. The rate constants k_2 and k_3 are probably no better than a factor of 6 to 8.

Discussion

It has been shown above that the reaction of BH_3 with C_2H_4 to form an adduct is being observed in the reaction zone. In the above the adduct has been assumed to be ethylborane. It may be argued that the species observed is a donor–acceptor complex such that the reaction might be represented as



Such a complex cannot be eliminated entirely, but there are two reasons for believing that the direct reaction

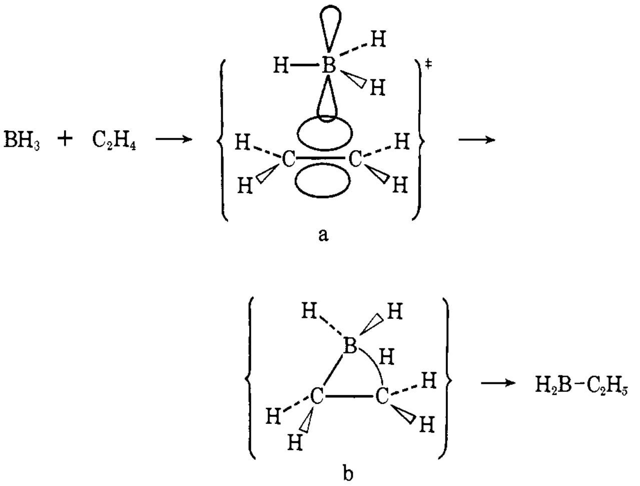
$$BH_3 + C_2H_4 \longrightarrow C_2H_5BH_2 \qquad (1)$$

is being observed. First, subsequent reactions are observed which can only be attributed in a simple fashion to the presence of $C_2H_5BH_2$. If most of the adduct were a donor–acceptor complex rather than the alkylborane, then the estimated rate constants for these subsequent reactions would become inordinately large. Second, the mass spectra of donor–acceptor complexes of borane have measurable parent ion intensities,[17] while the mass spectra of trialkylboranes have very small parent ion intensities (none is reported in ref 13). The measured m/e 42 ion intensity was very small and suggests that the species observed is not a donor–acceptor complex. Therefore, the measured rate constant and activation energy in all probability refer to the direct reaction of BH_3 with C_2H_4 to yield ethylborane.

If it is assumed that the high-pressure limiting rate constant is being measured, then the rate constant and activation energy measurements may be expressed in the form

$$k_1 = 10^{10.2} \exp(-2000/RT) \text{ l. mol}^{-1} \text{ sec}^{-1}$$

Combining the entropy of ethylborane, estimated by the procedures outlined by Benson,[18] with the known entropies of borane and ethylene yields the overall entropy for reaction 1. This, with the measured frequency factor, yields a value for the frequency factor for the unimolecular dissociation of ethylborane of *ca.* $10^{15.6}$ sec^{-1}. In the terminology of Eyring, *et al.*,[19] the activated complex for the association of BH_3 with C_2H_4 must be considered to be of the loose type. This conclusion holds even if the reaction being measured is partly in the falloff region. One such loose activated complex might be pictured as an interaction between the empty valence orbital of BH_3 and the filled orbital of C_2H_4. The formation of a boron–carbon bond and the transfer of a hydrogen atom to carbon must occur further along the reaction coordinate. The whole process can be envisioned as



where a is the activated complex and b is a representation of the system at some point further along the reaction coordinate in the direction of the product.

If the reaction has been measured at so low a pressure that the reaction is in the falloff region, then the rate constant given above is a lower limit of the high-pressure limiting rate constant. Crude estimates, in the manner of Benson,[18] of the lifetime of the energy-rich ethylborane molecule formed under our conditions indicate that the reaction is not appreciably in the falloff region. The observed high frequency factor and the positive activation energy support this conclusion.

The rate constants for the self-association of ethylborane (reaction 2) and the hydroboration of ethylborane (reaction 3) are also of considerable interest even though they are only estimates. The rate constant for the combination of two ethylborane molecules is one order of magnitude less than the estimated high-pressure limiting rate constant for the combination of two borane molecules.[1] This suggests that the presence of an ethyl substituent either sterically hinders the reaction or inductively lowers the reactivity of the free valence orbital. The reaction of ethylborane with ethylene is about 20 times slower than the reaction of borane with ethylene. This decrease in reaction rate could be due once again to either steric or inductive effects. This similarity in the effect of an ethyl substituent on the rates of the two reactions suggests a

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[17] S. A. Fridmann and T. P. Fehlner, *J. Phys. Chem.*, **75**, 2711 (1971).

[18] S. W. Benson, "Thermochemical Kinetics," Wiley, New York, N. Y., 1968.

[19] T. S. Ree, T. Ree, H. Eyring, and T. Fueno, *J. Chem. Phys.*, **36**, 281 (1962).

similarity in the interactions taking place in the activated complexes.

Finally, the results place some restrictions on the mechanism of the hydroboration reaction in more complex systems. If, in an overall hydroboration reaction, the mechanism involving BH_3 is favored over the direct reaction, then the barrier to reaction is not the reaction of BH_3 with the unsaturated species. For example, if the reaction of B_2H_6 with C_2H_4 proceeds through the intermediate BH_3, the reaction of BH_3 with C_2H_4 is not the slow step of the reaction. The slow step will probably be the production of BH_3. It should be kept in mind that, although an upper limit was placed on the rate constant for the direct reaction of B_2H_6 with C_2H_4, in a conventional thermal system (*e.g.*, ref 5) this upper limit is sufficiently high and the concentration of BH_3 is sufficiently low that it is still possible for the direct reaction to take place.

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Theory of the Rotational Barriers in Ethyl Fluoride and Ethane

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Abstract: *Ab initio* LCAO–MO–SCF wave functions have been computed with an atomic orbital basis set of double-ζ accuracy for the staggered and eclipsed conformations of ethyl fluoride and ethane. Total energy differences, ΔE_T, yield barriers of 2.59 and 2.58 kcal/mol for ethyl fluoride and ethane, respectively. These calculations are in reasonable agreement with the experimental result that barriers in these two molecules differ by about 10%. Our wave functions also substantiate and extend a previous conclusion that the origin of barriers is contained within the framework of the Hartree–Fock approximation. To obtain a more detailed understanding of the barrier mechanism, the total energy has been separated into its two competing and out-of-phase components: $V_{\text{attractive}} \equiv V_{\text{ne}}$ and $V_{\text{repulsive}} \equiv V_{\text{nn}} + T + V_{\text{ee}}$. Both ethyl fluoride and ethane are repulsive dominant. One result of the repulsive dominance is a small difference in dipole moment between staggered and eclipsed ethyl fluoride. A physical rationalization of the rough equality of these two barriers also follows from their common repulsive dominance. The sum of one-electron molecular orbital energies (Walsh criterion) is investigated as a means of predicting barrier magnitudes. This is shown to be reasonable for ethyl fluoride and ethane but not for some other molecules.

To understand the origin of internal rotation barriers, it has become apparent that it is necessary to generate and analyze *ab initio* wave functions for a considerable variety of molecules. In particular, an explanation of the surprisingly similar barriers displayed by ethyl fluoride and ethane is required if one is to provide a convincing barrier mechanism.

LCAO–MO–SCF *ab initio* wave functions have proved adequate for representing the principal features of barriers in ten other important molecules,[2] and wave functions at this level of approximation are shown here to be capable of producing reasonable magnitudes for the barriers in ethyl fluoride and ethane. This is the first report of an *ab initio* ethyl fluoride wave function, but there exist several ethane solutions of comparable accuracy to the one reported here.[3] Because of the small energy change involved in the barrier, it is absolutely essential to maintain perfectly balanced basis sets and identical computational machinery in generating wave functions for the two molecules.

I. Method and Basis Set

LCAO–MO–SCF wave functions were obtained *via* Roothaan's finite-expansion scheme. An atomic orbital basis set of double-δ quality was constructed from Gaussian functions. The carbon and fluorine s orbitals are made from the Gaussians given by Whitten[4] contracted into two groups, with the Gaussian of smallest exponent treated as one of the basis functions. The p's are a six-term Cartesian Gaussian set contracted to two basis functions, one of which is the Gaussian with smallest exponent, and the hydrogen 1s's are a four-term Gaussian set (contracted to a single function); both are taken from Huzinaga's tabulations.[5a] The H 1s was scaled so that it is equivalent to $\exp(-\sqrt{2}r)$. Atomic coordinates for the two molecules taken from the experimentally observed geometries[6] are listed in Table I.

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(1) (a) Princeton University; (b) Ford Motor Co.; Department of Chemistry, Bar Ilan University, Ramat-Gan, Israel.

(2) Methylamine, methanol, hydrogen peroxide, hydrazine, propane, and butane, L. C. Allen, *Annu. Rev. Phys. Chem.*, **20**, 315 (1969); acetaldehyde, R. B. Davidson and L. C. Allen, *J. Chem. Phys.*, in press; nitrosomethane, P. A. Kollman and L. C. Allen, *Chem. Phys. Lett.*, **5**, 75 (1970); propene and *cis*-fluoropropene, E. Scarzafava and L. C. Allen, *J. Amer. Chem. Soc.*, **93**, 311 (1971).

(3) Summarized in W. H. Fink and L. C. Allen, *J. Chem. Phys.*, **47**, 895 (1967).

(4) J. Whitten, *ibid.*, **44**, 359 (1966).

(5) (a) S. Huzinaga, *ibid.*, **42**, 1293 (1965). (b) It may be that the C_1C_2F angle undergoes a small opening or closing as the barrier is traversed. In ethane, geometrical distortion is known to modify the barrier height by no more than 0.1 kcal, and we have not tested this for ethyl fluoride.