

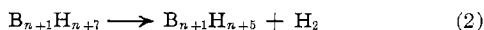
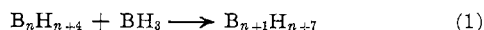
CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME,
NOTRE DAME, INDIANA 46556**Reactions of Borane (BH₃). V. Mass Spectrometric Observation of the Products of Addition to Diborane(6) and Pentaborane(9)**

BY S. A. FRIDMANN AND T. P. FEHLNER*

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The reaction of BH₃ with B₂H₆ and B₅H₉ in the gas phase has been examined utilizing a fast-flow system with mass spectrometric analysis. The addition products have been identified from their mass spectra, their phase spectra, variation in the reaction time, and variation in the reactant partial pressures. BH₃ reacts with B₂H₆ to produce a triborane while BH₃ reacts with B₅H₉ to produce a hexaborane. The relevance of these results to the interconversions of the boron hydrides is discussed.

Many investigators have shown that the formation of several of the higher hydrides of boron is consistent with a mechanism which involves borane (BH₃) addition to a stable hydride followed by hydrogen loss.^{1,2} The essence of such a mechanism can be represented by the general reactions



Since direct examination of the facile reactions of BH₃ in the gas phase is now possible,³ a systematic investigation of borane(3) reactions has been undertaken. This paper describes our investigation of the above reactions, for $n = 2$ and $n = 5$.⁴

The product of the above reaction for $n = 2$ is a triborane. The active intermediacy of this species in the conversion of diborane to higher hydrides has also been postulated numerous times¹ but, until recently,⁵ no direct physical evidence for its existence has been published. An objective of this study was to obtain evidence for the transient existence of this species.

Finally, we wished to compare the rate of reaction of BH₃ with stable hydrides with the rates of its reactions with other species⁶⁻⁹ in order to characterize further the reactivity of this species.

Experimental Section

The technique and procedures involved in the preparation of BH₃ and the utilization of modulated molecular beam sampling mass spectrometry in the reactions of BH₃ have been described in previous publications.⁶⁻⁹ In these studies⁶⁻⁸ the identification of products was quite straightforward as the signals involved were fairly large. In this study the observed signals were nearly at the limit of our detection system and the limit imposed by material consumption. In the optimum cases, *i.e.*, when the background ion intensity was small, we were able confidently to measure ion signals corresponding to 1 count/sec. To do so individual count times of 100 or 200 sec were used and multiple counts were taken. The final results are an average of numerous experiments on different days. Presumably, one could have im-

proved the counting statistics by still further increasing the counting times. Unfortunately, the use of a fast-flow system involves the consumption of rather large amounts of F₃PBH₃, the borane source (*ca.* 1 Torr l./sec). One side reaction in the preparation of BH₃ is the deposition of boron on the reactor walls with consequent constriction of the flow tube. This plus the safety hazard of large amounts of F₃PBH₃ put a practical limit on the achievable signal to noise ratio.

The general conditions of the experiments reported are as follows. Borane(3) was generated from F₃PBH₃ by thermal decomposition in a short section of the flow reactor. The temperature of the decomposition zone was 625°K and the residence time in this zone was *ca.* 0.4 msec. The position and shape of the axial temperature profile for this zone is illustrated at the top of Figure 1 of ref 6. The reaction zone, which included all of the flow reactor downstream of the decomposition zone, had a mean temperature of 450°K. The reaction time of BH₃ with the stable hydrides was varied from 0.1 to 0.5 msec by means of the movable probe through which the stable hydrides were introduced into the flow stream. For the qualitative identification experiments the stable hydrides were injected immediately downstream of the decomposition zone yielding a total reaction time of *ca.* 0.5 msec. Rate measurements were made by moving the probe, thereby defining a reaction zone consisting of the last 3 cm of the reactor. The mean BH₃ partial pressure in the reaction zone was varied from 0 to 17 mTorr while the stable hydride partial pressures were varied from 0 to 100 mTorr. The helium partial pressure was 4.7 Torr. F₃PBH₃ and B₂H₆ were prepared and purified as described previously.⁸ Pentaborane(9) was purchased from the Callery Chemical Co. and was fractionated once before using.

Results

Mass Spectra.—The initial evidence indicating the occurrence of reaction 1 and possibly reaction 2 for $n = 2$ resulted from the partial mass spectrum presented in Figure 1. Similar evidence is presented in Figure 2 for $n = 5$. The error bars represent the average deviation of all the experiments. The deviations are consistent with random errors expected on the basis of the counting statistics. The mass spectrometer was focused on a given m/e value using stable gases admitted to the flow stream during the experiment as mass markers. The ion intensities in the central portion of both spectra are those that depended on the pressure of both BH₃ and the stable hydride in the reaction zone. Because of the substantial background signals (which appear as noise in our system) below m/e 34 and above m/e 39 in Figure 1 and below m/e 68 and above m/e 75 in Figure 2, we were only able to obtain meaningful measurements on the central portion of the spectra. Ions were sought corresponding to tetraborane and pentaborane. Very small intensities were observed but these cannot account for the intensities observed in the region m/e 34–40. Unambiguous identification

(1) W. N. Lipscomb, "Boron Hydrides," W. A. Benjamin, New York, N. Y., 1963, p 154.

(2) M. F. Hawthorne, "The Chemistry of Boron and Its Compounds," E. L. Muetterties, Ed., Wiley, New York, N. Y., 1967, p 223.

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

(4) A preliminary report has appeared: S. A. Fridmann and T. P. Fehlner, *ibid.*, **93**, 2824 (1971).

(5) R. T. Paine, G. Sodeck, and F. E. Stafford, Abstracts, 162th National Meeting of the American Chemical Society, Washington, D. C., Sept 1971, No. INOR 2.

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

(7) T. P. Fehlner, *J. Amer. Chem. Soc.*, **93**, 6366 (1971).

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

(9) T. P. Fehlner, *Inorg. Chem.*, **11**, 252 (1972).

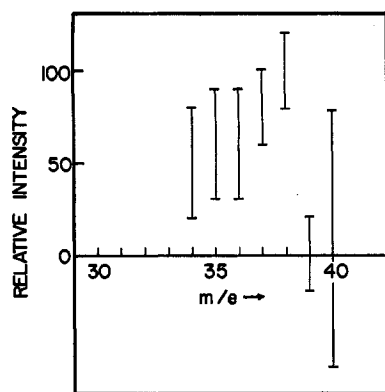


Figure 1.—Mass spectrum of the product of the reaction of BH_3 with B_2H_6 . A relative intensity of 100 corresponds to *ca.* 8 counts/sec. The spectrum is an average of a number of spectra taken at typical conditions of $(\text{BH}_3) = 14$ mTorr, $(\text{B}_2\text{H}_6) = 100$ mTorr, reaction time 0.5 msec, reaction temperature 450°K , and $(\text{He}) = 4.7$ Torr.

of the products is not possible on the basis of these partial spectra alone. However, in Figure 2 we have included the spectra of $\text{B}_6\text{H}_{10}^{10}$ and $\text{B}_6\text{H}_{12}^{11}$ and it may be seen that the spectrum we observe is consistent with what one would expect for a hexaborane.

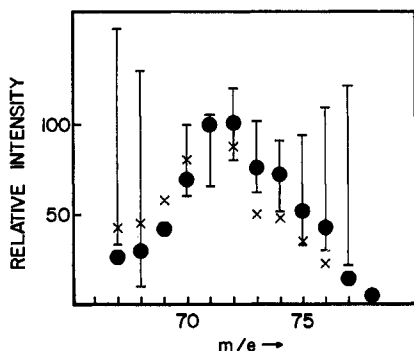


Figure 2.—Mass spectrum of the product of the reaction of BH_3 with B_5H_9 . A relative intensity of 100 corresponds to *ca.* 5 counts/sec. The spectrum is an average of a number of spectra taken at typical conditions similar to those given in the caption of Figure 1 with the exception that $(\text{B}_5\text{H}_9) = 100$ mTorr. The crosses represent the mass spectrum of $\text{B}_6\text{H}_{10}^{10}$ while the solid circles represent the mass spectrum of $\text{B}_6\text{H}_{12}^{11}$. The relative ion intensities at m/e 67, 68, 75, 76, and 76 have not been corrected for the B_5H_9 impurity discussed in the text.

Phase Spectra.—So that the identity of the products observed could be more firmly established the average molecular weights of the neutral progenitors of the m/e 38 ions produced in the reaction of BH_3 with B_2H_6 and of the m/e 71 ions produced in the reaction of BH_3 with B_5H_9 were measured by utilizing the fact that the phase shift between the reference signal and the ion signal is related to the average flight time in the molecular beam.¹² The results of these measurements are shown in Figures 3 and 4. For the reaction of BH_3 with B_2H_6 the relative phase of the m/e 38 ion peak was measured with respect to m/e 38 from allene (Figure 3) and m/e 58 from butane and m/e 27 from diborane (not shown). For the reaction with B_5H_9 the relative phase

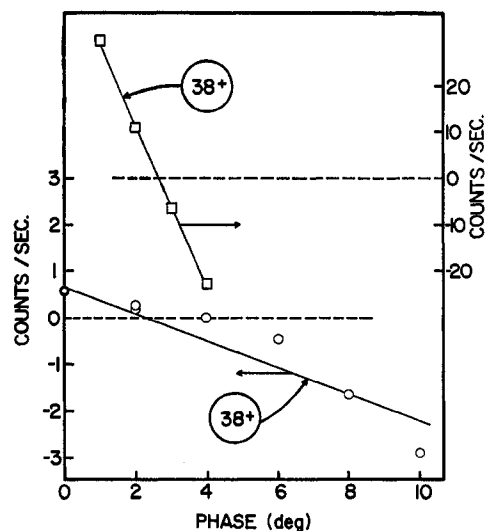


Figure 3.—Phase analysis of the m/e 38 ion produced by the ionization of the product of the reaction of BH_3 with B_2H_6 (circles) and the m/e 38 ion produced by the ionization of allene (squares). Counting times used were 100 sec.

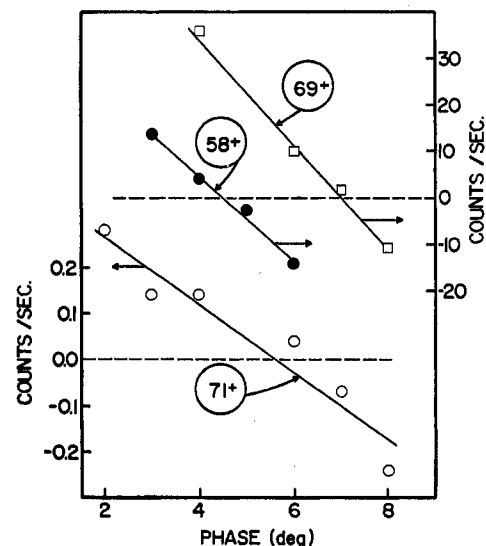


Figure 4.—Phase analysis of the m/e 71 ion produced by the ionization of the product of the reaction of BH_3 with B_5H_9 (open circles), the m/e 58 ion produced by the ionization of butane (closed circles), and the m/e 69 ion produced by the ionization of phosphorus trifluoride (squares). Counting times of 200 sec were used.

of the m/e 71 ion peak was measured with respect to m/e 58 from butane and m/e 69 from PF_3 (Figure 4). The results shown in Figures 3 and 4 are in the form of a plot of the difference of the signal at phase angle ϕ and the signal at phase angle $\phi + 180^\circ$ vs. the phase angle ϕ . The straight lines are least-squares fits of the data and the intercepts at zero intensity are taken to be the relative phases. From these data the molecular weight of the species giving rise to the product ions is 38 ± 10 in the case of B_2H_6 and 70 ± 10 in the case of B_5H_9 . The uncertainty is large but the measurements do lend confirmation to the identification of the addition products as a triborane and a hexaborane, respectively. The results definitely exclude the possibility that the ions attributed to a triborane result from the fragmentation of a pentaborane or higher hydride. They probably exclude the formation of these ions by

(10) S. G. Gibbons and I. Shapiro, *J. Chem. Phys.*, **30**, 1483 (1959).

(11) S. J. Steck, G. A. Pressley, F. E. Stafford, J. Dobson and R. Schaeffer, *Inorg. Chem.*, **9**, 2452 (1970).

(12) M. H. Boyer, E. Murad, H. Inami, and D. L. Hildenbrand, *Rev. Sci. Instrum.*, **39**, 26 (1968).

fragmentation of a tetraborane or by some unknown ion source process involving diborane. Analogous conclusions may be made concerning the ions attributed to a hexaborane.

Variation with Time.—The ion intensities attributed to reaction products were examined as a function of reaction time. The results for both the reaction of BH_3 with B_2H_6 and B_5H_9 are given in Figure 5. In

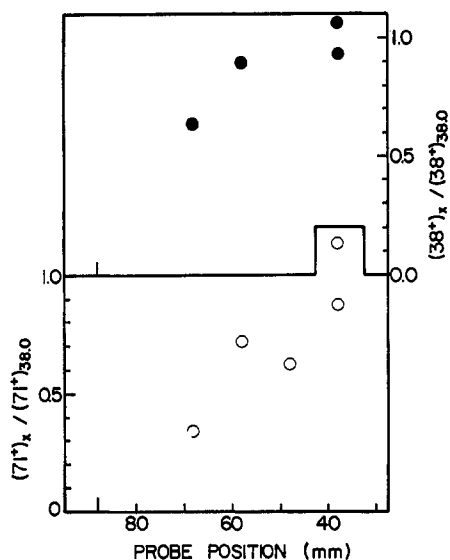


Figure 5.—Variation in the addition product ion signals with probe position (reaction time). The closed circles refer to m/e 38 from the reaction of BH_3 with B_2H_6 while the open circles refer to m/e 71 from the reaction of BH_3 with B_5H_9 . Counting times of 200 sec were used for m/e 38 and times of 100 sec for m/e 71.

both cases the ion intensities decrease with decreasing reaction time. The reaction time was varied by changing the position of injection of B_2H_6 or B_5H_9 with respect to the sampling orifice. The data for B_2H_6 in Figure 5 have not been corrected for the ubiquitous presence of B_2H_6 due to its formation as a by-product in the production of BH_3 , *i.e.*, by the self-association of BH_3 . The behavior of the product ion intensities with time is what would be expected if reaction is occurring with the added gas. These data are used below to estimate rate constants for the processes.

Variation with Partial Pressures.—The ion intensities attributed to addition products were examined both as a function of the partial pressure of BH_3 at constant stable hydride partial pressure and as a function of the partial pressure of stable hydride at constant BH_3 partial pressure. The results of these experiments are presented in Figures 6 and 7 for B_2H_6 and B_5H_9 , respectively. In both cases one sees the proper dependence of the addition product ion signals on the partial pressure of BH_3 and on the partial pressure of stable hydrides. The observed variations with the partial pressures of reactants indicate that the reactions being observed are indeed the addition of BH_3 to B_2H_6 and to B_5H_9 .

Besides this general observation these results deserve some individual comment. In the case of the reaction of BH_3 with B_2H_6 it was necessary to take into account the B_2H_6 produced concurrently with BH_3 during the pyrolysis of F_3PBH_3 . This was done in the following way. In order to measure the variation of addition

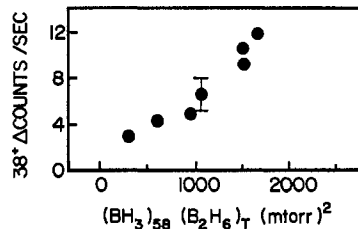
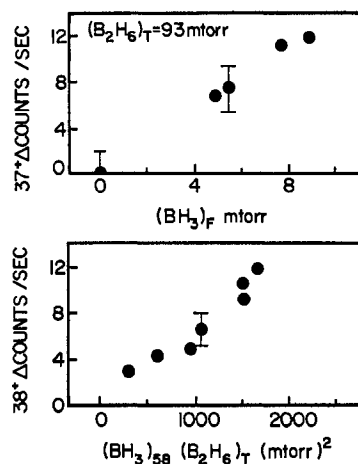


Figure 6.—Variation of the addition product ion signals for the reaction of BH_3 with B_2H_6 with BH_3 partial pressure at constant B_2H_6 partial pressure (top) and with B_2H_6 partial pressure at two constant BH_3 partial pressures (bottom). Count times of at least 200 sec were used.

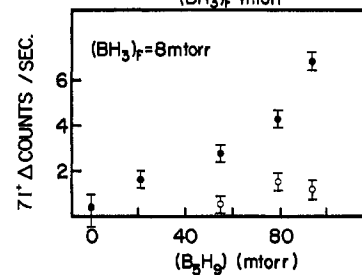
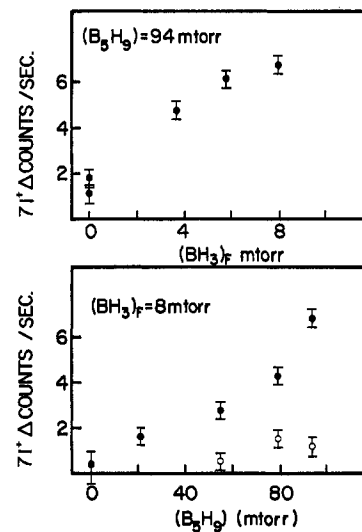


Figure 7.—Variation of the addition product ion signals for the reaction of BH_3 with B_5H_9 with BH_3 partial pressure at constant B_5H_9 partial pressure (top) and with B_5H_9 partial pressure at constant BH_3 partial pressure (bottom). The open circles in the bottom graph are points taken for $(\text{BH}_3) = 0$. Count times of 200 sec were used.

product with BH_3 at constant B_2H_6 , the mass flow of F_3PBH_3 was increased in steps and the mass flow of B_2H_6 decreased such that the partial pressure of B_2H_6 remained constant at 93 ± 5 mTorr (top of Figure 6). In order to illustrate the variation in product with B_2H_6 the ion intensity was plotted *vs.* the product of the BH_3 and total B_2H_6 partial pressures. In this case two levels of BH_3 were used (9 and 14 mTorr) and the diborane pressure was varied by a factor of 4 (bottom of Figure 6). The case of the reaction of BH_3 with B_5H_9 (Figure 7) did not require such considerations as no detectable B_5H_9 is produced in the pyrolysis of F_3PBH_3 . However, there was another complication which is clearly shown in Figure 7. The open circles in the lower plot of Figure 7 refer to the m/e 71 ion intensity observed for zero BH_3 partial pressure. This "background" is also evident in the nonzero intercept in the upper plot of Figure 7. The "background"

spectrum is crudely similar to that shown in Figure 2 and is attributed to a trace impurity in the pentaborane(9).

Rate Constant Calculations.—The data in Figure 5 may be used to calculate rate constants for the two addition reactions of BH_3 provided it is assumed that none of the addition products decompose and that a mass spectrometric sensitivity for the addition product is available. The stability of the addition products is discussed below. No calibrations could be carried out for a triborane; consequently, a sensitivity was estimated by simple extrapolation between the measured values for B_2H_6 and B_5H_9 . Although a sensitivity could have been obtained for both hexaboranes, this was not deemed necessary because of the large scatter in the best data obtainable. The sensitivity for hexaborane was assumed to be equal to that for pentaborane(9). Rate constants were then calculated from the approximate expressions

$$k_2 = \frac{\Delta(\text{B}_3)}{\Delta t} \frac{1}{(\text{BH}_3)(\text{B}_2\text{H}_6)_T}$$

$$k_5 = \frac{\Delta(\text{B}_6)}{\Delta t} \frac{1}{(\text{BH}_3)(\text{B}_5\text{H}_9)}$$

where $\Delta(\text{B}_3)/\Delta t$ and $\Delta(\text{B}_6)/\Delta t$ are the slopes of the curves in Figure 5 with appropriate calibration factors, B_3 and B_6 refer to the addition products, (BH_3) is the mean BH_3 partial pressure in the part of the flow tube used for the measurements, $(\text{B}_2\text{H}_6)_T$ is the total diborane partial pressure, and (B_5H_9) is the pentaborane partial pressure. With these approximations one calculates $k_2 = 3 \times 10^7$ l./mol sec and $k_5 = 10^7$ l./mol sec. These bimolecular rate constants must be considered as only order of magnitude estimates and will be lower limits if the addition products are not stable. Errors in our techniques have been discussed elsewhere.^{6,8}

Discussion

The evidence presented above allows two conclusions to be clearly drawn. First, BH_3 does easily add to stable hydrides. Second, a triborane does exist. We now wish to discuss some of the finer implications of this work but the reader should note that the complications that arise in this discussion do not affect these two important conclusions.

Reactions 1 and 2 for $n = 2$ and 5 may be structurally represented as shown in Figure 8 by utilizing the bonding nomenclature of Lipscomb.¹ Although the reaction of BH_3 with B_5H_9 is more complex than the reaction with B_2H_6 , it can also be represented as the insertion of BH_3 into a hydrogen-bridge bond followed either by the loss of H_2 to yield B_6H_{10} or by hydrogen rearrangement to yield B_6H_{12} . Unfortunately, our data do not directly indicate whether we are observing reaction 1 exclusively, a combination of (1) and (2), or the direct formation of $\text{B}_{n+1}\text{H}_{n+5}$ and H_2 from B_nH_{n+4} . We can, however, make some deductions based upon estimates of the heats of reaction for (1) and (2) and upon the known conditions for the observation of the addition products. Utilizing the average bond energies of Gunn, *et al.*,^{13,14} the heats of reaction for (1) and (2) were estimated for $n = 2$ and 5. These are given in Table I.

(13) S. R. Gunn and L. G. Green, *J. Phys. Chem.*, **65**, 2173 (1961).
 (14) S. R. Gunn and J. H. Kindsvater, *ibid.*, **70**, 1114 (1966).

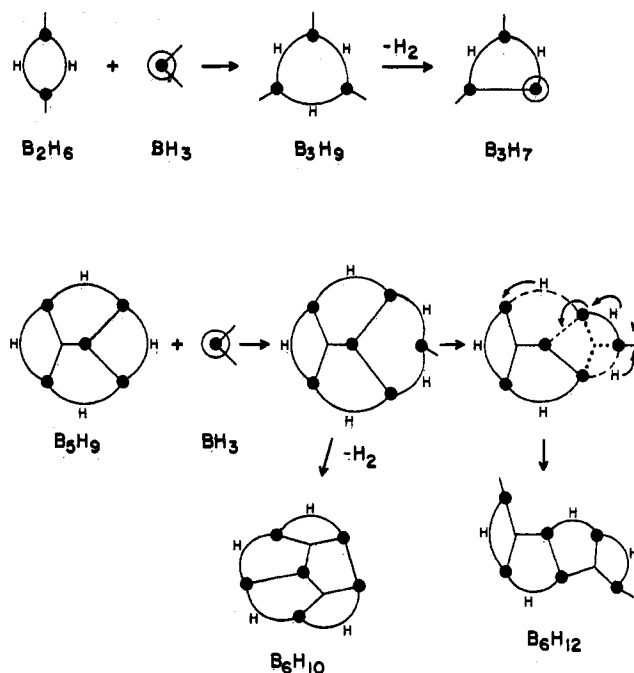


Figure 8.—A representation of a mechanism for the addition of BH_3 to B_2H_6 and to B_5H_9 . Each black dot represents a BH group, the straight lines represent additional hydrogens, the open circles represent unused valence orbitals, and the other symbols have their normal significance.

TABLE I
ESTIMATES OF THE HEATS OF REACTION FOR THE
ADDITION REACTIONS OF BH_3

n	(<i>styx</i>) _{reactant} ^b	(<i>styx</i>) _{product} ^b	ΔH_R , kcal/mol
	$\text{BH}_3 + \text{B}_n\text{H}_{n+4} = \text{B}_{n+1}\text{H}_{n+7}$		
2	2002	3003	-14
5	4120	4212	-6
	$\text{B}_{n+1}\text{H}_{n+7} \rightarrow \text{B}_{n+1}\text{H}_{n+5} + \text{H}_2$		
2	3003	2102	1
2	3003	2012	13
5	4212	4220	-6.9 ± 3^a

^a Measured.^{13,14} ^b Reference 1.

For both examples reaction 1 is exothermic as expected. The 2012 structure¹⁵ of B_3H_7 (illustrated in Figure 8) is also included in Table I as this structure may be the preferred one because of the large steric interaction of the BH_2 groups expected in the 2102 structure. Reaction 2 then is expected to be significantly endothermic for $n = 2$. In turn this suggests that B_3H_9 sits in a potential well that has a depth of at least 14 kcal with respect to re-forming BH_3 and B_2H_6 and a depth of at least 10 kcal with respect to forming B_3H_7 . As noted below there is probably a 6-kcal activation energy for the formation of B_3H_9 from BH_3 and B_2H_6 and it is quite probable that there is an activation energy for the reaction of B_3H_7 with H_2 . We suggest then that the triborane that we observe is B_3H_9 . This is reasonable in that a species will survive long enough for observation in our apparatus if the barrier to unimolecular decomposition is 15–20 kcal.

In contrast, for $n = 5$ both reactions 1 and 2 are exo-

(15) This structure does not satisfy the equations of balance¹ and is simply one representation of the bonding in this species. It is a possible representation because of the instability of triboranes. The 3011 structure is not considered, as recent work (I. R. Epstein and W. N. Lipscomb, *Inorg. Chem.*, **10**, 1921 (1971)) excludes this type of bonding arrangement.

thermic. As B_6H_{10} does not readily form from B_6H_{12} ,¹⁶ there must be a substantial activation energy for reaction 2. On the other hand B_6H_{12} lies only 6 kcal below $BH_3 + B_5H_9$. As the addition reaction probably has an activation energy less than or equal to 6 kcal, B_6H_{12} , if formed, would not be stable enough to survive our conditions long enough to be detected. This would be in conflict with the known stability of B_6H_{12} .¹⁶ Therefore we suggest that the hydrogen and boron rearrangement of the initial adduct illustrated in Figure 8 has a substantially higher barrier than the loss of an H_2 molecule. Thus it appears in this case that we are observing the direct reaction $BH_3 + B_5H_9 \rightarrow B_6H_{10} + H_2$.

As noted above these reactions of BH_3 do illustrate another aspect of the reactivity of this species. It is of interest to compare the rate constants for these reactions estimated above with those of other reactions of BH_3 that we have reported previously.⁶⁻⁹ Before doing so it is necessary to point out that in this study we cannot exclude the possibility of some type of surface involvement in the formation of the addition products. In previous studies we have argued that the reactions observed were homogeneous on the basis of the large magnitude of the rate constants.⁶ Here, however, products are observed only at very low levels, the rate constants are much smaller, and the arguments are much weaker. On the other hand the possibility

(16) A. L. Collins and R. Schaeffer, *Inorg. Chem.*, **9**, 2153 (1970).

of surface involvement does not affect the conclusion that the reaction of BH_3 with stable hydrides is substantially slower than the reaction with C_2H_4 ,⁷ $N(CH_3)_3$,⁸ and other species.^{6,9}

An interesting comparison is the rate of reaction of BH_3 with C_2H_4 and B_2H_6 . The rate constant for the former is at least 10^2 times larger than that for the latter.⁷ It is clear that BH_3 addition to a carbon-carbon double bond followed by rearrangement is favored over BH_3 insertion into a boron framework. It has been suggested that there is a relationship between reactivity and the interaction of highest filled orbitals and lowest unfilled orbitals.¹⁷ The highest filled orbital in C_2H_4 is a π MO ($1b_{2u}$) while in B_2H_6 it is a $1b_{2g}$ orbital, as the orbital corresponding to the π MO in C_2H_4 is the fourth lowest orbital in B_2H_6 .¹⁸ Assuming equal frequency factors for both reactions, the difference in rate constants would correspond to a difference in activation energies of 4 kcal. This in turn would indicate a total activation energy for the reaction of BH_3 with B_2H_6 of ca. 6 kcal.⁷

Acknowledgments.—This research was supported by the National Science Foundation under Grants No. GP 10199 and GP 28320. The aid of G. W. Mappes in setting up the apparatus is gratefully acknowledged. The helpful comments of the referees are appreciated.

(17) R. G. Pearson, *Accounts Chem. Res.*, **4**, 152 (1971).

(18) C. R. Brundle, M. B. Robin, H. Basch, M. Pinsky, and A. Bond, *J. Amer. Chem. Soc.*, **92**, 3863 (1970).

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Mixed Tetrahaloborate Ions. Detection and Study by Nuclear Magnetic Resonance¹

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BF_4^- , BCl_4^- , BBr_4^- , and BI_4^- undergo halogen exchange in methylene chloride solution to form the mixed tetrahaloborate ions, for which ¹⁹F and ¹¹B nmr data are presented. A previous report of very rapid halogen exchange in the BF_4^- - BCl_4^- system is incorrect. Only in the BF_4^- - BI_4^- system is halogen redistribution so rapid that separate nmr signals are not observed for the mixed-halogen anions. Exchange with methylene halide solvents gives rise to ternary-halogen species such as $BF_2Cl_2^-$. Additional methods of preparation of mixed tetrahaloborate anions are investigated. The nmr parameters of the mixed tetrahaloborate anions show trends which resemble those of the mixed boron trihalides. The trends can be interpreted in terms of the presence of boron-fluorine π bonding. The results of CNDO/2 calculations provide an alternative interpretation of the trends in chemical shifts. The ¹¹B and ¹⁹F chemical shifts of the tetrahaloborate anions are found to fit Malinowski's criteria of "pairwise additivity."

Introduction

Many boron-halogen compounds undergo halogen redistribution reactions to give mixed-halogen species. Although these reactions have been extensively studied for a number of types of boron-halogen compounds,²⁻⁵ relatively little is known about the mixed tetrahaloborate anions.⁵ Although there is evidence for the existence of several of the mixed tetrahaloborate ions in

crystalline solids, only the chlorotrifluoroborate ion appears to have been well characterized.^{5,6} A previous solution nmr study of the BF_4^- - BCl_4^- system in methylene chloride yielded only single averaged ¹⁹F and ¹¹B nmr peaks, the peak position depending on the relative amounts of fluorine and chlorine in the system, and a very rapid halogen exchange *via* the mixed tetrahaloborate ions was postulated.⁷ This behavior contrasted with the slower halogen-exchange reactions previously observed in BF_4^- ,⁸ the mixed

(1) Presented in part at the 54th Canadian Chemical Conference, Halifax, Nova Scotia, June 1971.

(2) J. C. Lockhart, "Redistribution Reactions," Academic Press, New York, N. Y., and London, 1970.

(3) J. C. Lockhart, *Chem. Rev.*, **65**, 131 (1965).

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(6) T. C. Waddington and F. Klanberg, *J. Chem. Soc.*, 2332 (1960).

(7) R. D. W. Kemmitt, R. S. Milner, and D. W. A. Sharp, *ibid.*, 111 (1963).

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