It should be noted that the only phosphorus-containing products formed in the reaction of phosphine with chloramine were polymeric phosphorus hydrides in contrast to the apparent red phosphorus formed in the reaction of phosphine with dimethylchloramine. This may be a result of the expected higher basicity of a dimethylamino group compared to that of an amino group.

Chloramine cleaves P–P bonds[12] and yields a mixture of aminophosphonium chlorides, their condensation products, and P–Cl compounds which are difficult to separate. It is probable that dialkylchloramines will also cleave P–P bonds. This may have been the difficulty encountered by Petrov[6] in characterizing the products obtained in his experiments. The products reported herein are obtained only when chloramine or dimethylchloramine is not in excess.

This type of reaction is currently being investigated with respect to hydrides of other elements and is being extended to include other substituted phosphines.

Acknowledgment.—The support of this research by the National Institutes of Health through Grant No. CA08263-03 with the University of Florida is gratefully acknowledged.

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Mass Spectrometric Study of Photoionization. XII. Boron Trifluoride and Diboron Tetrafluoride

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Mass spectra and photoion yield curves for the molecular and principal fragment ions of BF_3 and B_2F_4 are reported. The threshold regions only are measured for $B_2F_3^+$ and BF^+ from B_2F_4. These observations are intercompared in order to derive heats of formation of ions and radicals and bond dissociation energies. The boron–boron bond dissociation energy in B_2F_4 is calculated to be 431 kJ mol^{-1} (103 kcal mol^{-1}).

Introduction

Recent electron impact studies[1-4] on BF_3 have given remarkably concordant results of 15.5–15.7 eV for the ionization threshold of the molecule in spite of the relatively low intensity of that ion. Unfortunately, no extrapolated Rydberg series or photoionization measurements on BF_3 have been reported for comparison. The same authors[1-4] also report consistent values of about 16.2 eV for the threshold of the BF_2^+ ion in BF_3. The ionization energy of BF_2 necessary for the calculation of bond energies has not been measured directly. Steele, Nichols, and Stone[5] estimated $I(BF_2) = 9.4 \pm 0.1$ eV by subtracting an average[6] B–F bond energy of BF_3 from the electron impact value[1,2] of $A(BF_2^+)$. On the other hand, Margrave[7] used this value and electron impact results to calculate $\Delta H_f(BF_2)$, thus completing the circular argument.

Domalski and Armstrong[8] have stated that the thermochemistry of many boron compounds is dependent on the heat of formation of BF_3 and of the lower fluorides of boron. Thus the present study was undertaken in an attempt to obtain additional and more accurate values. To do so, the study includes measurements on B_2F_4 because of its obvious relationship to BF_3 and because it is one of the few volatile boron compounds containing a boron–boron bond. The necessity and advantage of a joint consideration of some of the experimental results for the two molecules will be apparent.

The mass spectrum of an apparently impure sample of B_2F_4 has been reported,[9] but no published data are available on ionization energies of this molecule. However, Gunn and Green[10] have investigated the heat of reaction for the chlorination of B_2F_4. The assumed equivalent reaction of $BF_3 + BCl_3$ results in a complex equilibrium mixture, and a B–B bond energy of 72.4 kcal mol^{-1} is calculated from the summation of heats of formation of the components. Unexpectedly, the same method resulted in a B–B bond energy of 79 kcal mol^{-1} for the less stable B_2Cl_4.

The following conversion factors are used in this report: 1 eV molecule^{-1} = 96.4870 kJ mol^{-1}; 1 kcal mol^{-1} = 4.1840 kJ mol^{-1}.

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Experimental Section

The photoionization yield curves and the threshold data were obtained by means of the combined vacuum ultraviolet monochromator and mass spectrometer described previously.[11] The continuum photon source, the photon intensities, ion count, and probable uncertainties are essentially as indicated in recent reports.[12]

The boron trifluoride was a commercial sample having a minimum purity of 99.5% as stated by the supplier. The mass spectrum at 584 Å (21.23 eV) confirmed this limit, showing no measurable impurities of significance to this work. It was used without further purification.

The diboron tetrafluoride was prepared by Dr. T. D. Coyle of the Inorganic Chemistry Section by fluorination of B_2Cl_4 with SbF_3 at −80°. The crude product was purified by trap-to-trap vacuum distillation. Material passing at −96° but retained at −125° was transferred to a borosilicate glass storage flask with a freeze-out tip. The material was maintained at liquid-nitrogen temperature throughout the course of study except for the very brief warmups required for sampling. An infrared spectrum of the purified material showed it to be free of boron chlorides. No BF_3 was detected and an upper limit of considerably less than 0.5% is assigned to this impurity.

Samples were introduced into the reservoir of the clean stainless steel inlet system of the mass spectrometer by sublimation from the solid. The vapor pressure in the flask and reservoir was never permitted to exceed 5 torr; thus the temperature remained well below −80°.

The mass spectrum is not a sensitive means of detecting small quantities of BF_3 in B_2F_4. Nevertheless, frequent checks of the mass spectrum of B_2F_4 were made to detect any changes. No significant variation in relative intensities of the appropriate ions was ever observed either during the course of an individual series of measurements or throughout the series of samples removed from the storage flask over a period of 10 days. Thus we assume that no change occurred in the initial composition as given by the infrared measurements.

Results and Discussion

BF_3.—The relative intensities of the positive ions in the mass spectrum of BF_3 obtained by means of 21.23-eV photons are given in Table I. The spectrum is obtained at a constant ion-accelerating voltage of 2.5 kV and the abundances of ions due to the ^{10}B and ^{11}B isotopes are added to give the monoisotopic spectrum.

TABLE I

MONOISOTOPIC MASS SPECTRA OF BF_3 AND B_2F_4 BY PHOTON ABSORPTION

Molecule	Ion	Rel abundance[a]
BF_3	BF_3^+	0.085
	BF_2^+	1.00
	BF^+	$\lesssim$0.005
B_2F_4	$B_2F_4^+$	0.10
	$B_2F_3^+$	1.00
	BF_3^+	0.008
	BF_2^+	0.76
	BF^+	0.30

[a] Measured at 584 Å (21.23 eV).

Incomplete evidence was obtained for the BF^+ ion as only one of the isotopic species could be detected. No negative ions were observed and it is estimated that the abundance of any ion-pair process is less than 0.002 relative to the BF_2^+ ion. These observations are consistent with previously published electron impact spectra.[2]

The photoionization efficiency curves for the BF_3^+ and BF_2^+ ions are shown in Figure 1. The BF^+ ion current is too weak to permit a threshold measurement using our continuum photon source. Wavelength in ångströms is plotted on the abscissa with equivalent energy in electron volts given at intervals. Ion counts per photon transmitted through the ion source are plotted in arbitrary units on the ordinate. The ordinate scale for the BF_2^+ ion is five times that of the BF_3^+ ion.

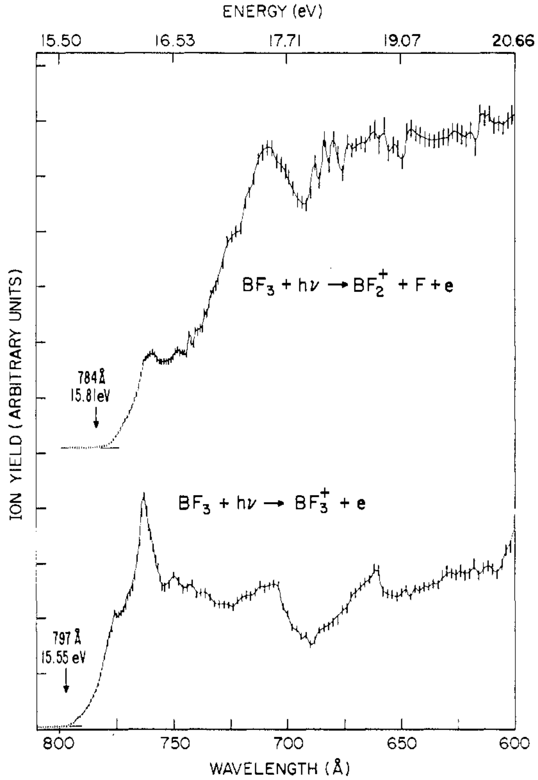

Figure 1.—Ionization efficiency curves for the BF_3^+ and BF_2^+ ions of BF_3.

The BF_3^+ ion yield curve exhibits a slowly rising onset at 797 Å (15.55 eV). Although in agreement with recent electron impact results, it probably represents an upper limit to the ionization threshold. Assuming it represents ΔH_0 = 358.6 kcal mol^{-1} for the reaction $BF_3 + h\nu \rightarrow BF_3^+ + e$ and adding the heat of formation[13] $\Delta H_f{}^\circ{}_0(BF_3) = -271.08$ kcal mol^{-1}, we obtain $\Delta H_f{}^\circ{}_0(BF_3^+) = 87.5$ kcal mol^{-1}. Thresholds and derived thermodynamic values are summarized in Table II.

The shape of the BF_3^+ ion curve near onset suggests the presence of numerous unresolved vibrational levels of the ion, probably resulting from severe distortion of the symmetric planar molecule upon ionization. Thus, it is reasonable to speculate that no identifiable Rydberg

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TABLE II

SUMMARY OF THRESHOLD ENERGIES AND THERMODYNAMIC PROPERTIES OF IONS AND RADICALS FROM BF_3 AND B_2F_4

Ion process	Threshold, eV[a]	Thermodynamic property
$BF_3 + h\nu \rightarrow BF_3^+ + e$	15.55 ± 0.04	$\Delta H_f{}^\circ{}_0(BF_3^+) = 87.5$ kcal mol^{-1}
$\rightarrow BF_2^+ + F + e$	15.81 ± 0.04	$\Delta H_f{}^\circ{}_0(BF_2^+) = 75.1$ kcal mol^{-1}
$B_2F_4 + h\nu \rightarrow B_2F_4^+ + e$	12.07 ± 0.01	$\Delta H_f{}^\circ{}_0(B_2F_4^+) = -65.2$ kcal mol^{-1}
$\rightarrow B_2F_3^+ + F + e$	15.40 ± 0.01	$\Delta H_f{}^\circ{}_0(B_2F_3^+) = -6.8$ kcal mol^{-1}; $I(B_2F_3) \approx 8.1$ eV
$\rightarrow BF_2^+ + BF_2 + e$	12.94 ± 0.01	$\Delta H_f{}^\circ{}_0(BF_2) = -120.2$ kcal mol^{-1}; $D_0(BF_2\text{–}BF_2) = 103.1$ kcal mol^{-1}; $I(BF_2) = 8.47$ eV
$\rightarrow BF_2^+ + BF + F + e$	18.0 ± 0.05	$\Delta H_f{}^\circ{}_0(BF) = -21.9$ kcal mol^{-1}
$\rightarrow BF^+ + BF_3 + e$	12.75 ± 0.01	$\Delta H_f{}^\circ{}_0(BF^+) = 221.6$ kcal mol^{-1}; $I(BF) = 10.56$ eV

[a] Estimated uncertainty.

series converging to the first ionization limit will be found in the absorption spectrum of the molecule.

The peaks in the wavelength region 765–730 Å are ascribed to autoionizing Rydberg levels of the molecule converging to electronically excited states of the ion. A second band of unresolved Rydberg levels appears in the 725–700-Å region. The increase in ion yield at about 690 Å (18.0 eV) followed by the relatively smooth continuum to 600 Å suggests an ionization threshold of an electronically excited state.

A weak but definite onset of the BF_2^+ ion appears at 784 Å (15.81 eV). This is considerably less than the electron impact values at about 16.2 eV, which is approximately identified with the first maximum of our curve at 760 Å. Taking our threshold of 15.81 eV (364.6 kcal mol^{-1}) to be the ΔH_0 for the reaction $BF_3 + h\nu \rightarrow BF_2^+ + F + e$ and summing the necessary heats of formation[13] we obtain $\Delta H_f{}^\circ{}_0(BF_2^+) = 75.1$ kcal mol^{-1}. As noted earlier, no direct measurement of the ionization energy of BF_2 is known. However, following Steele, *et al.*, we can immediately approximate it by calculating the *average* B–F bond dissociation energy of BF_3 from recent thermodynamic values[13] and subtracting this (6.7 eV) from the threshold energy. Assuming the first B–F bond to be stronger than the average bond, we obtain the upper limit, $I(BF_2) < 9.1$ eV. It is interesting to note that Price and coworkers[14] have compared ionization and dissociation energies of various isoelectronic species and estimated $D(BF_2\text{–}F) = 7.0$ eV. Applied to our threshold value of BF_2^+, this gives an estimated value of $I(BF_2) = 8.8$ eV. Further conclusions concerning this quantity are deferred until the discussion section on BF_2^+ from B_2F_4.

B_2F_4.—Relative intensities of the positive ions of B_2F_4 are recorded in Table I. There is no evidence for $B_2F_2^+$ and B_2F^+ ions or any negative ions at present sensitivity, and an estimated upper limit to relative intensities is 0.005. The mass spectrum shows no trace of the various impurity ions tabulated by Gayles and Self.[9] With those exceptions, the relative intensities of the principal ions are similar.

The weak BF_3^+ ion is interpreted as a rearrangement ion such as is frequently observed in mass spectra. As such, it limits the usefulness of the spectrum as a means of detecting incipient decomposition of B_2F_4.

The ion yield curves for the $B_2F_4^+$ and BF_2^+ ions from threshold to 600 Å and the initial portions of the $B_2F_3^+$, BF_2^+, and BF^+ ions are shown in Figures 2 and 3, respectively. The thresholds are summarized in Table II. Curves were not taken with customary detail because of the scarcity of sample. However, sufficient observations were made on $B_2F_4^+$ and BF_2^+ to obtain evidence of interesting features.

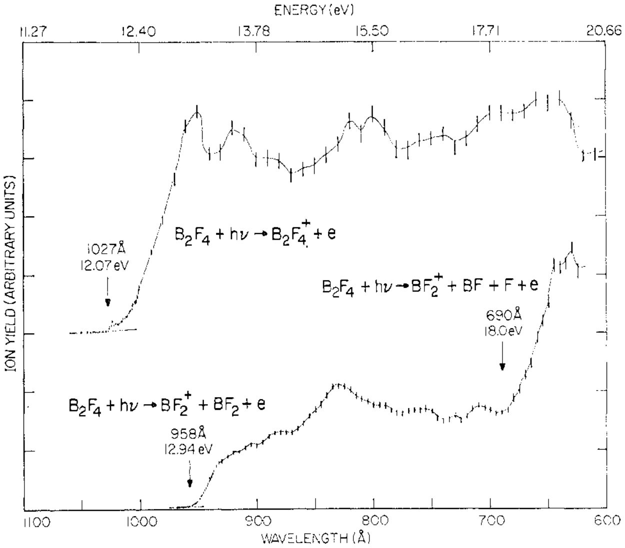

Figure 2.—Ionization efficiency curves for the $B_2F_4^+$ and BF_2^+ ions of B_2F_4.

The $B_2F_4^+$ ion exhibits a definite onset at 1027 Å (12.07 eV). No previous measurement of this ionization threshold is known. It is considerably lower than the ionization energy of BF_3 or of F_2. It is quite similar however to $I(B_2) = 12.1$ eV derived from electron impact studies of diborane.[15] Adding the heat of formation[13] $\Delta H_f{}^\circ{}_0(B_2F_4) = -343.5$ kcal mol^{-1} to our threshold value gives $\Delta H_f{}^\circ{}_0(B_2F_4^+) = -65.2$ kcal mol^{-1}. The remainder of the ion yield curve shows evidence for unresolved autoionization of Rydberg levels in the molecule. However, there is no important increase in the ionization continuum that could be ascribed to the onset of excited ionic states.

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(14) W. C. Price, T. R. Passmore, and D. M. Roessler, *Discussions Faraday Soc.*, **35**, 201 (1963).

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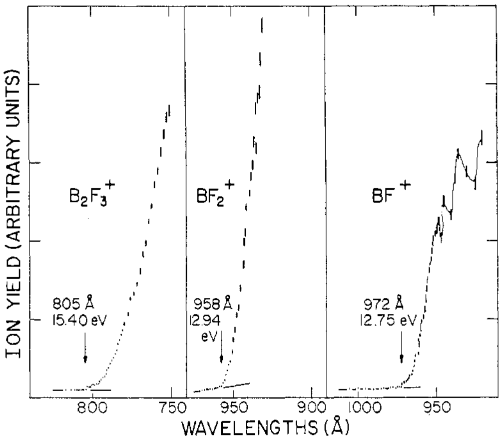

Figure 3.—Initial portions of the ionization efficiency curves for the $B_2F_3^+$, BF_2^+, and BF^+ ions of B_2F_4.

The ion yield curve of the BF_2^+ ion is also shown in Figure 2 with the initial onset region replotted on a more sensitive scale in Figure 3. The latter figure shows a definite onset at 958 Å (12.94 eV). Some evidence for autoionization appears in the wavelength region 840–700 Å (Figure 2). At about 690 Å (18.0 eV) the ion yield curve rises sharply indicating the onset of a second ionization process. The energy interval of 5.1 eV (118 kcal mol^{-1}) is in sufficient agreement with the dissociation energy D(FB–F) = 123 kcal mol^{-1} derived from Knudsen-cell studies by Hildenbrand and Murad[16] to identify the dissociative ionization processes to be those given in Table II. Therefore, we conclude that the lower energy onset of 12.94 eV (298.4 kcal mol^{-1}) represents the ΔH_0 for the reaction $B_2F_4 + h\nu \rightarrow BF_2^+ + BF_2 + e$. Assuming no excess energy in this reaction and accepting $\Delta H_f{}^\circ{}_0(BF_2^+) = 75.1$ kcal mol^{-1} from the BF_3 measurements, we calculate $\Delta H_f{}^\circ{}_0(BF_2) = -120.2$ kcal mol^{-1}, from which we immediately obtain $D_0(F_2B\text{–}BF_2) = 103.1$ kcal mol^{-1}. This is greater than the value of 72.4 kcal mol^{-1} obtained by Gunn and Green[10] but is consistent with the relative stability of B_2F_4 compared with B_2Cl_4. We also note that our B–B bond value is similar to the B–C bond strength of ~100 kcal mol^{-1} obtained by Steele, *et al.*,[5] from alkyl-substituted boron difluorides.

The difference between $\Delta H_f{}^\circ{}_0(BF_2^+)$ and $\Delta H_f{}^\circ{}_0(BF_2)$ is, of course, the ionization energy of BF_2. The above values for these properties permit us to calculate $I(BF_2) = 195.3$ kcal mol^{-1}, or 8.47 eV, and, for the BF_3 molecule, $D(BF_2\text{–}F) = 169.3$ kcal mol^{-1}, or 7.34 eV. These are generally in agreement with, but much more accurate than, the previous estimates of these properties outlined earlier. Bond dissociation energies of BF_3 are summarized in Table III.

The second onset of the BF_2^+ ion at 18.0 eV (Figure 2) is ascribed to the process $B_2F_4 + h\nu \rightarrow BF_2^+ + BF + F + e$. If we assume 18.0 eV (415.1 kcal mol^{-1}) represents ΔH_0 for the reaction, we can then calculate $\Delta H_f{}^\circ{}_0(BF) = -21.9$ kcal mol^{-1} and, obviously, $D_0(BF) = 173.6$ kcal mol^{-1}, or 7.53 eV. This is somewhat lower than $D_0 = 7.85 \pm 0.15$ eV reported by Hildenbrand and Murad and the spectroscopic value of 185 kcal mol^{-1} favored by Barrow.[17] Although the uncertainty in our value is difficult to assess, in the absence of systematic error we estimate about 1 kcal mol^{-1} or 0.04 eV. This is indicated by a comparison of the sum of the individual B–F bond dissociation energies obtained from BF_3 and B_2F_4 with the heat of atomization of BF_3 calculated from the appropriate heats of formation. As shown in Table III, the agreement is quite satisfactory, although, of course, correct distribution among the bonds is not proved.

TABLE III

INDIVIDUAL BOND DISSOCIATION ENERGIES IN BF_3 AS DETERMINED FROM BF_3 AND B_2F_4

Bond		Energy eV	Energy kcal mol^{-1}
BF_2–F		7.34	169.3
BF–F[a]		5.10	117.6
B–F[a]		7.53	173.6
	Total	19.97	460.5
	$BF_3 \rightarrow B + 3F$	19.92[b]	459.5[b]

[a] Determined for B_2F_4 and assumed the same in BF_3. [b] Calculated from heats of formation.[13]

The BF^+ ion of B_2F_4 (Figure 3) shows a very definite onset at 972 Å (12.75 eV). The low energy indicates a very stable neutral product. If the threshold energy (294.0 kcal mol^{-1}) is taken to be the ΔH_0 for the reaction $B_2F_4 + h\nu \rightarrow BF^+ + BF_3 + e$, we calculate $\Delta H_f{}^\circ{}_0(BF^+) = 221.6$ kcal mol^{-1}. Subtracting the above heat of formation of BF gives $I(BF) = 243.5$ kcal mol^{-1}, or 10.56 eV. This differs considerably from the ionization energies of the isoelectronic molecules N_2 (15.75 eV) and CO (14.01 eV). However, the assumed process is very probably correct as any other would result in a still lower I(BF).

The value of $\Delta H_f(BF^+)$ precludes the observations of BF^+ from BF_3 at 584 Å, assuming molecular fluorine as the neutral product. However, we have some evidence for the ion in BF_3 and we cannot rule out the possibility that $\Delta H_f(BF^+)$ may be an upper boundary to the true value.

The $B_2F_3^+$ ion of B_2F_4 shows a very definite onset at 805 Å (15.40 eV). Assuming that 355.1 kcal mol^{-1} is the ΔH_0 for the reaction $B_2F_4 + h\nu \rightarrow B_2F_3^+ + F$, we calculate $\Delta H_f{}^\circ{}_0(B_2F_3^+) = -6.8$ kcal mol^{-1}. Assuming that $D(B_2F_3\text{–}F)$ is approximately the same as $D(BF_2\text{–}F)$, we estimate $I(B_2F_3) = 8.1$ eV. This is very near our value of $I(BF_2)$. Unfortunately, these last results cannot be compared with independent measurements.

While we assume the near equivalence of the first B–F bond dissociation energy in the neutral molecules, it should be noted that the dissociation energy for the same bond calculated for the ions BF_3^+ and $B_2F_4^+$ differs widely (6.0 and 76.8 kcal mol^{-1}, respectively). Fundamentally, this is related to the very different ionization energies of the two molecules and suggests

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(17) R. F. Barrow, *Trans. Faraday Soc.*, **56**, 952 (1960).

that ionization of B_2F_4 occurs through removal of an electron much more closely associated with the B–B skeleton than with the B–F bond.

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Strong Hydrogen Bonds. IV. The $B_2H_7^-$ Species[1,2]

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Tetraethylammonium borohydride reacts at −78.5° with diborane to form $(C_2H_5)_4NB_2H_7$. At 0° hydrogen is also produced in a 1:10 mol ratio of H_2 to $(C_2H_5)_4BH_4$. Calorimetric studies allow an estimate of -31 ± 8 kcal/mol to be made for the minimum enthalpy of formation of the hydrogen bond in $B_2H_7^-$. This large enthalpy for an electron-deficient hydrogen bond is interpreted as showing that the lone pair usually deemed necessary for hydrogen-bond formation may actually be antibonding in character.

The $B_2H_7^-$ species was first postulated by Brown, Tierney, and Stehle[3] to account for the deviation from Henry's law of the pressure of B_2H_6 in contact with a solution of $NaBH_4$ in diglyme.[4] They proposed a structure for this anion involving a single hydrogen bridge bond. This is the only structure consistent with the equations of balance[5] for this species.

Our interest in the $B_2H_7^-$ species centered about the hydrogen-bond energy of the electron-deficient BHB bond. In order to obtain a value for this energy, a first requirement is a simple borohydride salt which reacts with diborane with no solvent present. A solid $NaB_2H_7\cdot$diglyme had previously been isolated but attempts to remove the diglyme had been unsuccessful.[6] Lipscomb[7] had suggested that the $B_2H_7^-$ ion may not exist in the absence of solvent stabilization.

If the role of the diglyme is to solvate the sodium ion, rather than the $B_2H_7^-$ ion, removal of the diglyme should produce a salt which could increase its lattice energy greatly through the loss of diborane

$$NaB_2H_7(s) \longrightarrow NaBH_4(s) + 0.5B_2H_6(g)$$

According to this viewpoint, the reverse of the above reaction does not occur (in the absence of solvent), because the energy needed to expand the $NaBH_4$ lattice in order to accommodate the $B_2H_7^-$ species which would be formed is greater than the energy which is released through the formation of the $B_2H_7^-$ species. The situation appears to be analogous to the failure of NaBr to add HBr or NaI to add HI although such reactions do occur when tetraalkylammonium salts are used instead of sodium salts. The ionic radius[8] of BH_4^- is 2.03 Å, compared to 1.95 Å for Br^- and 2.16 Å for I^-.

Adams[9] was unable to prepare KB_2H_7 either in solution or as a solid, probably because the difference in lattice energies of KBH_4 and KB_2H_7 is large and the energy of coordination of potassium ion with diglyme is small.

It would appear that stable compounds containing the $B_2H_7^-$ species could be synthesized if the size of the cation were adjusted so that the lattice energies of MBH_4 and MB_2H_7 were comparable. The tetraalkylammonium cation seemed to be most suitable for this purpose. It was expected that very little lattice expansion would be needed to insert a "BH_3" unit into the lattice of a tetraalkylammonium borohydride. The preparation of a $B_2H_7^-$ compound under these circumstances would indicate that stabilization by solvation is not essential.

Experimental Section

Tetraethylammonium borohydride (Aldrich Chemical Co.), reported purity 97.5%, was used as received. Diborane was prepared from the reaction of concentrated H_2SO_4 with KBH_4 (Callery Chemical Co.) under conditions described by Jolly.[10]

Pressure–composition isotherms were obtained at −78.5 and 0° in a greaseless section of the vacuum line.[11] At −78.5° (see Figure 1) the reaction between B_2H_6 and $(C_2H_5)_4NBH_4$ evolved a

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[11] For a general discussion of vacuum-line techniques see R. T. Sanderson, "Vacuum Manipulation of Volatile Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948.