states and their relative positions are analogous in the two molecules,[20] but emission from borazine excited at 1849 Å has not been detected,[11] indicating little if any radiative decay. Other examples in the literature for which vibrational mechanisms have been proposed are the photodecompositions of 1,3-cyclohexadiene and 1,3,5-hexatriene.[21] In each case H_2 and benzene were produced. Moreover, the H_2 production was quenched by increased pressures in the system. Evidence here too indicated an internal conversion from the initially produced short-lived singlet state to a vibrationally excited ground state that eliminates the H_2. As we reported earlier, based on our evidence one can eliminate the borazine triplet from major participation in the mechanism. We therefore suggest that the species $B_3N_3H_6'$ is a vibrationally "hot" ground electronic state and that H_2 elimination occurs by a process involving the distribution of internal energy. Vibrational relaxation through collisions lowers the energy below a threshold and thereby quenches the elimination reaction. The fact that Ar is an efficient quencher indicates that the elimination reaction has a relatively high energy threshold. The relative amounts of H_2 and D_2 produced in the photolysis of an equimolar mixture of $B_3N_3H_6$ and $B_3N_3D_6$ suggest a frequency factor in the rate which is isotope dependent.[22]

We have noted that the photochemical exchange reaction between $B_3N_3H_6$ and $B_3N_3D_6$ (equimolar mixture) that produces the species $B_3N_3D_5H$ and $B_3N_3H_5D$ has a quantum yield of the order of 4–5 for an initial total pressure of 1.5 mm. These quantum yields (Table I) may be slightly low because we have not considered the more highly mixed species such as $B_3N_3D_4H_2$ and $B_3N_3H_4D_2$ which are formed by subsequent reactions of $B_3N_3D_5H$ and $B_3N_3H_5D$. Figure 2 indicates that at a constant integrated intensity (I_at) the pressure of $B_3N_3D_5H$, and hence its quantum yield, increases linearly with the total pressure of the equimolar mixture. In addition, the approximately constant value of the exchange quantum yield (Table I) over a factor of 2 in I_at indicates that the product yield may be first order in intensity. It would follow that

$$d(B_3N_3D_5H)/dt \propto I_aP_T \qquad (8)$$

However, it is clear that as the total pressure of the mixture is increased, the pressure of the product $B_3N_3D_5H$ cannot continue to rise indefinitely for the same I_at. The curve must eventually level off since the quantum yield should reach a limiting value.

On the basis of the evidence presented, we conclude that following initial excitation of the borazine to the $^1E'$ state by the 1849-Å radiation internal conversion occurs to a vibrationally excited ground-state molecule that can subsequently undergo two modes of reaction: (1) decomposition by elimination of H_2 with a relatively high energy threshold and (2) exchange reaction(s) with a relatively low threshold. Hydrogen elimination is reduced with increased pressures in the system, while the exchange reaction rate in the pressure range studied increases with borazine pressure. This increase and the high quantum yield observed suggest an exchange process of low activation energy. The results of these experiments may also be significant in the interpretation of the photochemical reactions of borazine with a second reagent.

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(20) S. D. Peyerimhoff and R. J. Buenker, *Theor. Chim. Acta*, **19**, 1 (1970).

(21) R. Srinivasan, *J. Chem. Phys.*, **38**, 1039 (1963).

(22) It has been determined that the extinction coefficients of borazine and perdeuterioborazine at 1849 Å are 980 and 658 l. mol^{-1} cm^{-1}, respectively. Therefore, in the equimolar mixture the $B_3N_3D_6$ absorbs only about 40% of the light. However, it is noted that the low D_2:H_2 ratio observed following photolysis cannot be completely explained by a consideration of relative light absorption. The experiments with cyclohexane provide a more striking illustration of this fact.

Chemical Ionization Mass Spectrometry of Selected Boron Hydrides

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Abstract: Chemical ionization mass spectra for diborane, tetraborane, pentaborane(9), pentaborane(11), and hexaborane(10) in methane have been obtained. The boron hydrides B_2H_6, B_4H_{10}, and B_5H_{11} are ionized by dissociative proton transfer and hydride abstraction to form $(M - 1)^+$ ions, while B_5H_9 and B_6H_{10} react with a number of hydrocarbon ions to form $(M + 1)^+$ species, and high molecular weight complexes. A new technique for determining the relative ordering of the proton affinities of gaseous molecules is described. The proton affinity of B_5H_9 is found to be intermediate between that for H_2O and H_2S or PA(B_5H_9) = 167 ± 6 kcal/mol. Hexaborane(10) with a proton affinity in excess of 186 kcal/mol is a stronger base than B_5H_9. Proton-transfer reactions of $B_4H_9^+$ indicate that the proton affinity of B_4H_8 is 184 ± 6 kcal/mol. The proton affinity of B_2H_6 is estimated to be 145 kcal/mol. The second-order rate constant for the protonation of B_5H_9 by CH_5^+ is 1.93×10^{-9} cm^3/(molecule sec).

Chemical ionization mass spectrometry is now established as a useful technique capable of providing information on proton affinities of gaseous molecules. Although the technique has been employed extensively for study of organic compounds, its potential for investigation of inorganic systems has not yet been fully developed. For several reasons it appeared to us that the boron hydrides constitute an interesting class of

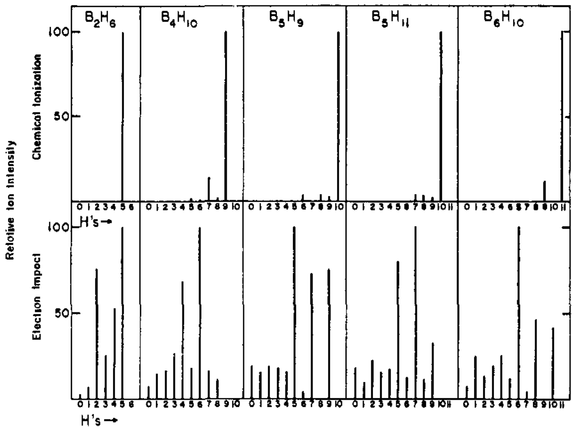

Figure 1. Comparison of CI mass spectra (upper) with EI mass spectra (lower) of some boron hydride molecules. CI spectra obtained for samples of composition methane/boron hydride = 200:1. For B_2H_6, B_4H_{10}, B_5H_9, B_5H_{11}, and B_6H_{10}, the P_s (source pressure) was 0.62, 0.77, 0.87, 0.41, and 0.45 mm, respectively.

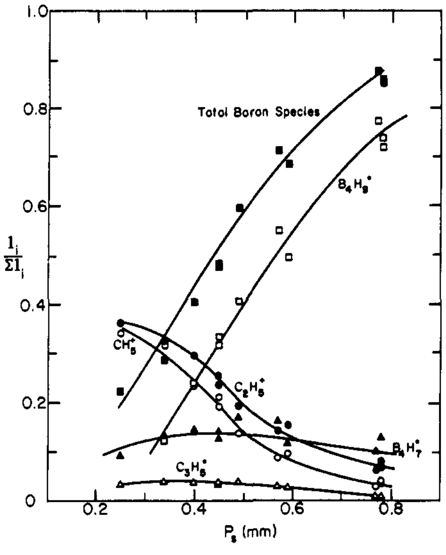

Figure 2. Effect of source pressure on the relative intensity of ions in the CI spectra of B_4H_{10} in CH_4. Sample composition, CH_4: B_4H_{10} = 200:1.

inorganic compounds for study by chemical ionization methods. First of all, aside from the general interest in the chemistry of these compounds, the simplest members of the group are well characterized to provide a basis for a systematic study. Secondly, it was anticipated that the relative tendency for these compounds to act as proton acceptors would reflect features of chemical bonding and structure unique to the boron hydrides. In this paper we discuss results of a chemical ionization study of the five simplest boron hydrides, B_2H_6, B_4H_{10}, B_5H_9, B_5H_{11}, and B_6H_{10}.

Experimental Section

The chemical ionization source used in these experiments was designed according to the description given by Field and Munson.[1] The ion box with inner dimensions of 0.438 × 0.438 in. contained a 0.002 × 0.313 in. entrance slit for the electron beam from the filament compartment and a 0.002 × 0.344 in. exit slit for the ion beam. The gas entered the source through a small stainless-steel tube brazed onto the ion box. This was connected by a piece of flexible Teflon tubing to a glass inlet tube. The filament housing was external to the ion box and open to the vacuum system. The source was equipped with a repeller to maintain a field strength of 11.6 V/cm. The electron bombardment energy was maintained at 100 V and the positive ion acceleration potential was held at 3000 V. The source reached a temperature of 100 ± 3° during operation. This source was found to be superior to the one described earlier.[2] Primary ions CH_3^+ and CH_4^+ from methane were completely consumed by chemical ionization reaction at a source pressure of 0.24 mm.

Gas mixtures were prepared by adding an excess of carrier gas to a bulb containing a small quantity of the boron hydride whose pressure was measured on a silicone oil manometer.

The boron hydrides B_2H_6 (B_2D_6),[3] B_4H_{10},[4] B_5D_9,[5] B_5H_{11},[4] and B_6H_{10}[6] were prepared by standard procedures. Pentaborane(9) was obtained from Callery Chemical Co. Purity of the boron hydrides was checked by mass spectra, infrared spectra, and glpc.[7]

In some experiments for proton affinity measurements, three-component gas mixtures were investigated. These mixtures contained an excess of carrier gas, a small quantity of boron hydride, and a small quantity of a second proton acceptor. The latter compounds included C_2H_4, $C_2H_2D_2$ (unsymmetrical), D_2O, C_3D_6 (propene-d_6), C_4H_8 (1-butene), H_2S, C_3H_4 (allene), and acetone. To simplify interpretation of proton-transfer reactions, one or two of the components were partially or totally deuterated.

Results

Chemical ionization mass spectra (CI) were obtained for five boron hydrides using methane as the source of reactant ions (CH_5^+, $C_2H_5^+$, and $C_3H_5^+$). Monoisotopic mass spectra[8] obtained by chemical ionization are compared in Figure 1 with published spectra[9] obtained by electron impact (EI). Under electron impact the boron hydrides fragment severely by loss of H or H_2 units. One immediate observation is that the principal mass grouping is simplified considerably in the CI spectra. A second obvious feature of the spectra in Figure 1 is that the compounds with dihydro terminal groups, B_2H_6, B_4H_{10}, and B_5H_{11} ionize by hydride abstraction and dissociative proton transfer, while the compounds with a monohydro terminal group, B_5H_9 and B_6H_{10}, ionize by proton transfer. Major features of the CI spectra will be discussed briefly.

CD_4-B_2H_6. In this system, CD_4 was used in place of CH_4 to avoid possible confusion arising from superposition of $C_2H_3^+$ and $B_2H_5^+$ which have the same nominal masses. The only boron species, $B_2H_5^+$, comprised 60% of the total intensity at a source pressure of 0.62 mm. Thermochemical calculations[10] indicate that the only possible exothermic reactions leading to $B_2H_5^+$ are (a) dissociative proton transfer with CH_5^+

$$CH_5^+ + B_2H_6 \longrightarrow B_2H_5^+ + CH_4 + H_2 \qquad (1)$$
$$\Delta H = -15.6 \text{ kcal/mol}$$

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(2) R. F. Porter, and J. J. Solomon, *ibid.*, **93**, 56 (1971).

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

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(5) B_5D_9 was prepared by the pyrolysis of B_2D_6.

(6) J. L. Boone and A. B. Burg, *J. Amer. Chem. Soc.*, **81**, 1766 (1959).

(7) W. R. Deever, E. R. Lory, and D. M. Ritter, *Inorg. Chem.*, **8**, 1263 (1969).

(8) The monoisotopic spectra were calculated by employing a least-squares technique: J. I. Brauman, *Anal. Chem.*, **38**, 607 (1966).

(9) A. P. I. Project 44, "Tables of Mass Spectral Data," Nos. 30–32, 333, and 334. Electron energy = 70 V.

(10) Heats of formation obtained from J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Herron, K. Draxl, and F. H. Field, "Ionization Potentials, Appearance Potentials, and Heats of Formation of Gaseous Positive Ions," NSRDS-NBS, No. 26, U. S. Government Printing Office, Washington, D. C., 1969.

Table I. Chemical Ionization Mass Spectra of Alkane–Pentaborane(9) Mixtures

Ionic species	$I_i/\Sigma_i I_i$ ($\times$ 100): CH_4 + B_5H_9[a]	C_2H_6 + B_5H_9[b]	n-C_4H_{10} + B_5H_9[c]
CH_5^+	3.63		
H_3O^+	0.14		
$C_2H_3^+$	0.19		
$C_2H_4^+$	0.27	2.80	
$C_2H_5^+$	6.65	1.08	
$C_2H_6^+$		0.11	
$C_3H_3^+$		0.38	0.44
$C_3H_5^+$	1.29	0.82	
$C_3H_7^+$		3.75	1.56
? ($C_2H_5OH_2^+$)		1.49	
$C_4H_7^+$		0.76	
$C_4H_8^+$			6.85
$C_4H_9^+$		7.42	45.74
$C_4H_{10}^+$		0.36	1.55
$B_5H_6^+$		0.86	
$B_5H_7^+$	1.41		
$B_5H_9^+$	3.06	31.87	7.34
$B_5H_{10}^+$	53.39	5.29	
$C_5H_{11}^+$		0.60	4.04
$CB_5H_7^+$	0.99		
$CB_5H_8^+$	0.23		
$CB_5H_9^+$	1.14		
$CB_5H_{10}^+$	16.64	6.70	
$CB_5H_{11}^+$	0.46		
$CB_5H_{12}^+$	1.09	1.07	
$C_2B_5H_9^+$		0.95	
$C_2B_5H_{10}^+$	0.47		
$C_2B_5H_{11}^+$	0.08	2.66	
$C_2B_5H_{12}^+$	5.15	19.13	30.21
$C_2B_5H_{14}^+$		1.88	
$C_3B_5H_{12}^+$	0.45	1.41	
$C_3B_5H_{14}^+$	3.27	6.98	2.27
$C_3B_5H_{16}^+$		1.64	

[a] $CH_4:B_5H_9$ = 200:1; P_s = 0.65 mm. [b] $C_2H_6:B_5H_9$ = 200:1; P_s = 0.62 mm. [c] n-$C_4H_{10}:B_5H_9$ = 200:1, P_s = 0.40 mm.

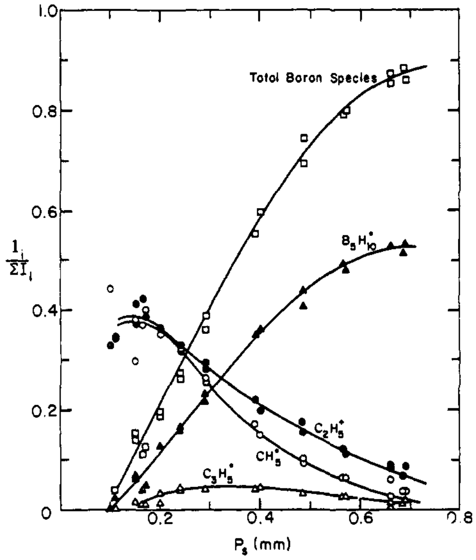

Figure 3. Effect of source pressure on the relative intensity of major ions in the CI spectra of B_5H_9 in CH_4. Sample composition, $CH_4:B_5H_9$ = 200:1.

and (b) hydride abstraction with $C_2H_5^+$

$$C_2H_5^+ + B_2H_6 \longrightarrow B_2H_5^+ + C_2H_6 \qquad (2)$$
$$\Delta H = -15.7 \text{ kcal/mol}$$

CH_4–B_4H_{10}. The effect of source pressure on the relative intensities of ions in the CH_4–B_4H_{10} system is illustrated in Figure 2. At the highest pressure, the intensity of $B_4H_9^+$ is 80% of the total ionization. The relative intensity of $B_4H_7^+$ remains nearly constant at about 10% throughout the pressure range (0.2–0.8 mm). Possible reactions to form $B_4H_9^+$, which accounts for 85% of all boron hydride species in the system, include dissociative proton transfer (CH_5^+ + B_4H_{10}) and/or ($C_2H_5^+$ + B_4H_{10}) and hydride abstraction ($C_2H_5^+$ + B_4H_{10}).

CH_4–B_5H_{11}. In this system, $B_5H_{10}^+$ is the major ion produced by chemical ionization. At a source pressure of 0.41 mm, $B_5H_{10}^+$ comprises 92% of the total intensity due to boron hydride ions. This ion is probably also formed by dissociative proton transfer and hydride abstraction with CH_5^+ and $C_2H_5^+$, respectively.

Alkane–B_5H_9 and Alkane–B_6H_{10}. The variations of the relative intensity of the major ions in the CH_4–B_5H_9 system as a function of source pressure are shown in Figure 3. It is evident that CH_5^+ and $C_2H_5^+$ are reacting with B_5H_9 to form $B_5H_{10}^+$. Above a source pressure of 0.34 mm, $B_5H_{10}^+$ is the dominant ion in the spectrum. It comprises more than 50% of the total intensity at a source pressure of 0.65 mm. (See Figure 3 and Table I.) Other boron hydride ions are low in abundance, as shown in Figure 1.[11] At the highest pressures, boron species contribute about 90% of the ionic species. Table I indicates that nearly 30% of the ionic boron species are complexes of carbon, hydrogen, and boron. The major complex species are $CB_5H_{10}^+$ (~16%), $C_2B_5H_{12}^+$ (~5%), and $C_3B_5H_{14}^+$ (~3%). In order to elucidate probable structures for the complex ionic species, chemical ionization spectra were obtained for CD_4–B_5H_9 and CH_4–B_5D_9 mixtures. Table II summarizes the information that was obtained. It is evident from comparison of the CH_4–B_5H_9 and CD_4–B_5H_9 systems that each of the species $CB_5H_{12}^+$, $C_2B_5H_{12}^+$, and $C_3B_5H_{14}^+$ contains five hydrogens originating from a hydrocarbon ion. A plausible set of equations to account for the formation of these ionic species is

$$CH_5^+ + B_5H_9 \longrightarrow CB_5H_{12}^+ + H_2 \qquad (3)$$
$$C_2H_5^+ + B_5H_9 \longrightarrow C_2B_5H_{12}^+ + H_2 \qquad (4)$$
$$C_3H_5^+ + B_5H_9 \longrightarrow C_3B_5H_{14}^+ \qquad (5)$$

These species are probably (M ± 1)$^+$ alkylpentaborane(9) ions. Comparison of the CH_4–B_5H_9 and CH_4–B_5D_9 mixtures shows that the species $CB_5H_{10}^+$ is formed from the addition of a CH group to B_5H_9. The following reactions are postulated to account for the formation of this ion, which may be a protonated form of the CB_5H_9 (*nido*-carborane) ion.

$$CH_5^+ + B_5H_9 \longrightarrow CB_5H_{10}^+ + 2H_2 \qquad (6)$$

and/or

$$C_2H_5^+ + B_5H_9 \longrightarrow CB_5H_{10}^+ + CH_4 \qquad (7)$$

The dominant ion in the chemical ionization spectrum of C_4H_{10} at source pressures employed in this study is $C_4H_9^+$. This ion does not protonate B_5H_9 (see Table I). Apparently, $C_4H_9^+$ reacts with pentaborane(9) to form $C_2B_5H_{12}^+$ and C_2H_6. The only boron hydride ion present in the CI spectrum is $B_5H_9^+$, which must be formed mainly by a charge-transfer reaction with a hydrocarbon ion. Thermochemical calcu-

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[11] $B_5H_{10}^+$ is ~91% of all boron hydride ions at the highest source pressures.

Table II. Results of Isotopic Labeling Experiments for Identification of Complex Species in CI Spectra of Methane–Pentaborane(9) Mixtures

CH_4–B_5H_9	CD_4–B_5H_9	CH_4–B_5D_9	Probable species
$B_5H_{10}^+$	$B_5H_9D^+$ $B_5H_{10}^+$	$B_5D_9H^+$ $B_5D_{10}^+$	Protonated pentaborane (9)
$CB_5H_{10}^+$	$CB_5H_9D^+$ $CB_5H_8D_2^+$	$CB_5HD_9^+$	Protonated form of CB_5H_9 carborane
$CB_5H_{12}^+$	$CB_5H_7D_5^+$		Protonated methylpentaborane(9)
$C_2B_5H_{12}^+$	$C_2B_5H_7D_5^+$		$(M - 1)^+$ of ethylpentaborane (9)
$C_3B_5H_{14}^+$	$C_3B_5H_9D_5^+$		$(M - 1)^+$ of propylpentaborane(9)

lations[12] indicate that the only possible exothermic or thermoneutral charge-transfer reaction is

$$n\text{-}C_4H_{10}^+ + B_5H_9 \longrightarrow B_5H_9^+ + n\text{-}C_4H_{10} \qquad (8)$$
$$\Delta H = \sim -1 \text{ kcal/mol}$$

The chemical ionization mass spectrum of pure ethane consists of $C_2H_4^+$, $C_2H_5^+$, and small contributions of $C_2H_6^+$, $C_3H_5^+$, $C_3H_9^+$, and $C_4H_9^+$. The data of Table I indicate that the predominant reaction in the C_2H_6–B_5H_9 system is charge transfer to produce $B_5H_9^+$. A thermodynamic analysis of the ions present in this system indicates that both $C_2H_4^+$ and $C_2H_6^+$ may take part in this reaction. Since $B_5H_9^+$ comprises nearly 30% of the total ion intensity at high source pressures, we conclude that $C_2H_4^+$ is the major source for charge transfer. Protonation of B_5H_9 also occurs in this system. The likely protonating reagent is $C_2H_5^+$ (see later discussion).

Comparison of chemical ionization mass spectra of alkane–B_5H_9 with alkane–B_6H_{10} reveal some obvious differences in behavior. In Table III we indicate monoisotopic spectra for C_3H_8–B_6H_{10} and C_4H_{10}–B_6H_{10} experiments. In both of these cases there is evidence of proton transfer to B_6H_{10} from the predominant hydrocarbon ions, $C_3H_7^+$ and $C_4H_9^+$, respectively. In the C_3H_8–B_6H_{10} system, the intense ion appearing in the mass range 114–119 is attributed mainly to a complex, $C_3H_7B_6H_{10}^+$. Another ion, $C_4H_9B_5H_7^+$, with similar isotopic distribution and the same nominal mass, could arise from a reaction of $C_4H_9^+$ and B_5H_9 which may be present as a minor impurity in the B_6H_{10} sample. However, since $C_4H_9B_5H_7^+$ is not observed as a major species in the C_4H_{10}–B_5H_9 system, its contribution is considered negligible. Another important difference in the B_5H_9 and B_6H_{10} systems is that in the formation of some complex species, hydrocarbon ions tend to add to B_6H_{10} but react with B_5H_9 by elimination of H_2. As we note later, this probably reflects the observation that B_6H_{10} is a stronger base than B_5H_9.

Table III. Chemical Ionization Spectra of C_3H_8–B_6H_{10} and C_4H_{10}–B_6H_{10} Mixtures

C_3H_8–B_6H_{10}[a]		C_4H_{10}–B_6H_{10}[b]	
Ion	I_i/I_t	Ion	I_i/I_t[c]
$C_3H_3^+$	1.8	$C_3H_3^+$	1.9
$C_3H_7^+$	10.5	$C_4H_8^+$	2.5
$C_4H_9^+$	1.0	$C_4H_9^+$	34.9
$B_6H_{10}^+$	5.9	$B_5H_9^+$	2.4
$B_6H_{11}^+$	15.5	$B_6H_9^+ + B_6H_{10}^+$	10.2
$C_6H_{13}^+$	2.6	$B_6H_{11}^+$	25.9
$C_2B_5H_{12}^+$ $CB_6H_{13}^+$	7.0	$C_2B_5H_{12}^+$ $CB_6H_{13}^+$	11.1
$C_3B_5H_{14}^+$ $C_2B_6H_{15}^+$	6.2		
$C_4B_5H_{16}$ $C_3B_6H_{17}^+$	38.7	$C_3B_5H_{14}^+$ $C_2B_6H_{15}^+$	3.9
Σ(residual ions)	10.8	Σ(residual ions)	7.2

[a] P_s = 0.30 mm, C_3H_8:B_6H_{10} = 150:1. [b] P_s = 0.22 mm, C_4H_{10}:B_6H_{10} = 100:1. [c] Units are percentages.

Proton Affinities of B_5H_9, B_6H_{10}, and B_4H_8. To obtain upper and lower boundaries on the proton affinities of B_5H_9 and B_6H_{10}, it is necessary to observe reactions in which these molecules are proton acceptors and other reactions in which the protonated boron hydrides are proton donors. We have investigated by chemical ionization a series of two-component and three-component reaction mixtures. In two-component mixtures, the ionized carrier gas is the source of the proton and the occurrence of proton transfer to the boron hydride is noted by changes in intensity profiles as the source pressure is increased. Since boron hydrides are likely to react thermally with strong bases, this technique is somewhat limited in selection of carrier gases. We therefore devised a procedure utilizing mixtures containing an excess of methane, a small quantity of boron hydride (∼1.0%), and a small quantity of a second proton acceptor (∼1.0%). The two types of reactions investigated were (1) reactions of a proton donor (RH^+) with a boron hydride (BH) through the sequence

$$CH_5^+ + R \longrightarrow RH^+ + CH_4 \qquad (9)$$
$$RH^+ + BH \longrightarrow BH_2^+ + R \qquad (10)$$

and (2) reactions of protonated boron hydride (BH_2^+) with a proton acceptor (R) through the sequence

$$CH_5^+ + BH \longrightarrow BH_2^+ + CH_4 \qquad (11)$$
$$BH_2^+ + R \longrightarrow RH^+ + BH \qquad (12)$$

These reactions involve transfer of a proton between stable molecules, and therefore no competing process is usually possible. Haney and Franklin[13a] postulated that the nonoccurrence of reactions of this type is sufficient evidence for their endothermicity. In Tables IV and V, we summarize results of these experiments for B_5H_9 and B_6H_{10}. It should be noted that to postulate the occurrence of a reaction an effect indicated as "pertinent" in Tables IV and V had to be obvious and of reasonable magnitude. For example, in the CH_4–D_2O–B_5H_9 sequences the intensity of $B_5H_9D^+$ increased to over 40% of the total intensity of the protonated B_5H_9 species and to over 20% of the total

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(12) IP(B_5H_9) = 10.54 ± 0.1 eV: C. B. Murphy, Jr., and R. E. Enrione, *Int. J. Mass Spectrom. Ion Phys.*, 5, 157 (1970). Reference 10 was used for heats of formation of other species.

(13) (a) M. A. Haney and J. L. Franklin, *J. Phys. Chem.*, 73, 4328 (1969); (b) *J. Chem. Phys.*, 50, 2028 (1969).

Table IV. Chemical Ionization Data for Two- and Three-Component Gas Mixtures Containing B_5H_9

Reaction mixture	Reaction comp	Reaction sequences	P_s, mm	Pertinent observations	$PA(B_5H_9)$,[a] kcal/mol
$CH_4–B_5H_9$	200:1	$CH_5^+ + B_5H_9 \rightarrow B_5H_{10}^+ + CH_4$	0.87	Occurs extensively; CH_5^+ consumed $(I_{B_5H_{10}^+}/I_{CH_5^+})_5 = 5.4 \times 10^3$	$\gg 126 \pm 1$[b]
$CH_4–B_5D_9$	200:1	$CH_5^+ + B_5D_9 \rightarrow B_5D_9H^+ + CH_4$ $B_5D_9H^+ + B_5D_9 \rightarrow B_5D_{10}^+ + B_5D_8H$		Occurs extensively; sources of D^+	
		$B_5D_9H^+ + CH_4 \rightarrow CH_4D^+ + B_5D_8H$ $(B_5D_{10}^+)$ (B_5D_9)	0.50	Not observed; $I_{CH_4D^+}$ not detectable above ^{13}C contribution from CH_5^+	$\gg 126 \pm 1$
$CH_4–C_2H_4–B_5D_9$	226:1.0:1.4	$CH_5^+ + B_5D_9 \rightarrow B_5D_9H^+ + CH_4$ $B_5D_9H^+ + B_5D_9 \rightarrow B_5D_{10}^+ + B_5D_8H$		Occurs extensively; sources of D^+	
		$B_5D_9H^+ + C_2H_4 \rightarrow C_2H_4D^+ + B_5D_8H$ $(B_5D_{10}^+)$ (B_5D_9)	0.70	Not observed; $I_{C_2H_4D^+}$ not detectable above ^{13}C contribution from $C_2H_5^+$	$>160 \pm 2$
$CH_4–C_2H_2D_2–B_5H_9$	28.6:1.0:0.29	$CH_5^+ + B_5H_9 \rightarrow B_5H_{10}^+ + CH_4$		Occurs extensively	
		$CH_5^+ + C_2H_2D_2 \rightarrow C_2H_3D_2^+ + CH_4$		Occurs extensively; source of D^+	$>160 \pm 2$
		$C_2H_3D_2^+ + B_5H_9 \rightarrow B_5H_9D^+ + C_2H_3D$	0.50	Observed; $(I_{BD^+}/I_{BH^+})_s = 0.05$	
$CH_4–D_2O–B_5H_9$	154:1.0:1.0	$CH_5^+ + B_5H_9 \rightarrow B_5H_{10}^+ + CH_4$		Occurs extensively	
		$CH_5^+ + D_2O \rightarrow D_2OH^+ + CH_4$ $D_2OH^+ + D_2O \rightarrow D_3O^+ + DOH$		Occurs extensively; sources of D^+	
		$D_2OH^+ + B_5H_9 \rightarrow B_5H_9D^+ + DOH$ (D_3O^+) (D_2O)	0.60	Observed; $(I_{BD^+}/I_{BH^+})_s = 0.81$	$>165 \pm 3$[c]
$CH_4–C_3D_6–B_5D_9$ (propene)	73:1.0:0.45	$CH_5^+ + C_3D_6 \rightarrow C_3D_6H^+ + CH_4$ $C_3D_6H^+ + C_3D_6 \rightarrow C_3D_7^+ + C_3D_5H$ $\rightarrow C_6D_{12}H^+$		Occurs extensively; source of $C_3D_7^+$	
		$CH_5^+ + B_5D_9 \rightarrow B_5D_9H^+ + CH_4$ $B_5D_9H^+ + B_5D_9 \rightarrow B_5D_{10}^+ + B_5D_8H$		Occurs extensively; sources of D^+	
		$B_5D_9H^+ + C_3D_6 \rightarrow C_3D_7^+ + B_5D_8H$ $(B_5D_{10}^+)$ (B_5D_9)	0.44	Observed; $(I_{C_3D_7^+}/I_{C_3D_6H^+})_s - (I_{C_3D_7^+}/I_{C_3D_6H^+})_b = 0.38$	$<180 \pm 2$[d]
$CD_4–C_4H_8–B_5H_9$ (1-butene)	134:1.0:1.2	$CD_5^+ + B_5H_9 \rightarrow B_5H_9D^+ + CD_4$ $B_5H_9D^+ + B_5H_9 \rightarrow B_5H_{10}^+ + B_5H_8D$		Occurs extensively; sources of H^+	
		$CD_5^+ + C_4H_8 \rightarrow C_4H_8D^+ + CD_4$		Occurs extensively	
		$C_4H_8D^+ + C_4H_8 \rightarrow C_4H_9^+ + C_4H_7D$		Occurs extensively; source of $C_4H_9^+$	
		$B_5H_9D^+ + C_4H_8 \rightarrow C_4H_9^+ + B_5H_8D$ $(B_5H_{10}^+)$ (B_5H_9)	0.63	Observed; $(I_{C_4H_9^+}/I_{C_4H_8D^+})_s - (I_{C_4H_9^+}/I_{C_4H_8D^+})_b = 0.46$	$<174 \pm 5$[e]
$CH_4–H_2S–B_5D_9$	130:1.0:0.65	$CH_5^+ + B_5D_9 \rightarrow B_5D_9H^+ + CH_4$ $B_5D_9H^+ + B_5D_9 \rightarrow B_5D_{10}^+ + B_5D_8H$		Occurs extensively; sources of D^+	
		$CH_5^+ + H_2S \rightarrow H_2SH^+ + CH_4$		Occurs extensively	
		$B_5D_9H^+ + H_2S \rightarrow H_2SD^+ + B_5D_8H$ $(B_5D_{10}^+)$ (B_5D_9)	0.49	Observed; $(I_{H_2SD^+}/I_{H_2SH^+})_s = 0.49$	$<170 \pm 3$[c]

[a] Unless otherwise specified, thermochemical data used in this paper were taken from J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Herron, K. Draxl, and F. H. Field, "Ionization Potentials, Appearance Potentials, and Heats of Formation of Gaseous Positive Ions," NSRDS–NBS No. 26, U. S. Government Printing Office, Washington, D. C., 1969. s refers to three-component sample CH_4–R–B; b refers to two-component blank (CH_4–R) of the same composition as sample. [b] M. A. Haney and J. L. Franklin, *J. Phys. Chem.*, **73**, 4328 (1969). A recent photoionization study of methane has determined $PA(CH_4) = 129 \pm 3$ kcal/mol: W. A. Chupka and J. Berkowitz, *J. Chem. Phys.*, **54**, 4256 (1971). [c] Haney and Franklin, footnote *b* and *J. Chem. Phys.*, **50**, 2028 (1969). [d] Using ΔH_f (*sec*-$C_3H_7^+$) = 190 kcal/mol. [e] Using ΔH_f(*sec*-$C_4H_9^+$) = 192 kcal/mol; see footnote *a*. Most stable straight-chain species.

Table V. Chemical Ionization Data for Two- and Three-Component Gas Mixtures Containing B_6H_{10}

Reaction mixture	Comp	P_s, mm	Pertinent reactions	Observations	$PA(B_6H_{10})$, kcal/mol
n-$C_4H_{10}–B_6H_{10}$	100:1	0.22	$C_4H_9^+ + B_6H_{10} \rightarrow B_6H_{11}^+ + C_4H_8$	Occurs extensively	$>173 \pm 1$[a]
$C_3H_8–B_6H_{10}$	100:0.67	0.30	$C_3H_7^+ + B_6H_{10} \rightarrow B_6H_{11}^+ + C_3H_6$	Occurs extensively	$>180 \pm 2$[b]
$CD_4–C_3D_6–B_6H_{10}$	100:1.3:0.34	0.30–0.50	$CD_5^+ + B_6H_{10} \rightarrow B_6H_{10}D^+ + CD_4$	Occurs extensively	
			$B_6H_{10}D^+ + C_3D_6 \rightarrow C_3HD_6^+ + B_6H_9D$	Not observed; $I_{B_6H_{10}D^+}/I_t = 0.52$, but $I_{C_3HD_6^+}/I_t = 0.02$ and is insensitive to P_s	$>180 \pm 2$[b]
$PH_3–B_6H_{10}$	100:1	0.20	$PH_4^+ + B_6H_{10} \rightarrow B_6H_{11}^+ + PH_3$	Occurs extensively; $I_{B_6H_{11}^+}/I_t = 0.74$	$>186 \pm 1$[c]

[a] Calculated using thermochemical data for *sec*-butyl ion and *trans*-2-C_4H_8 (most stable straight-chain species). [b] Calculated using values for heats of formation of propene and *sec*-$C_3H_7^+$. [c] M. A. Haney and J. L. Franklin, *J. Phys. Chem.*, **73**, 4328 (1969). A recent icr study has determined the proton affinity of phosphine; $PA(PH_3) = 185 \pm 4$ kcal/mol: D. Holtz, J. L. Beauchamp, and J. R. Eyler, *J. Amer. Chem. Soc.*, **92**, 7045 (1970).

ionization. Thus, since the quantity of D_2O in the sample was only 0.65% on a molar basis, it is unlikely that a significant fraction of $B_5H_9D^+$ could arise by proton transfer from primary ions formed from D_2O. In situations where a reaction is postulated not to occur, the criterion for judgment was a low intensity of a hypothetical reaction product that was insensitive to source pressure. When a protonation reaction occurs to an appreciable extent, the reverse reaction is probably undetectable. Experiments with $CH_4–C_2H_2D_2–B_5H_9$ show that D^+ transfer from $C_2H_3D_2^+$ to B_5H_9 occurs, while experiments with $CH_4–C_2H_4–B_5D_9$ show that D^+ transfer from $B_5D_9H^+$ to C_2H_4 does not occur. Similarly, $C_3H_7^+$ does not protonate B_5H_9, but C_3D_6 is a D^+ acceptor from $B_5D_9H^+$. Brackets for the proton affinity of B_5H_9 are set between $PA(H_2O)$ and $PA(H_2S)$

Table VI. Chemical Ionization Data for Three-Component Gas Mixtures Containing B_4H_{10}

Reaction mixture	Comp	P_s, mm	Pertinent reaction	Observations	$PA(B_4H_8)$, kcal/mol
CD_4–B_4H_{10}–C_3H_4	100:1.0:1.2	0.36–0.60	$B_4H_9^+ + C_3H_4 \rightarrow C_3H_5^+ + B_4H_8$	Reaction occurs; $(I_{C_3H_5^+}/I_{C_3H_4D^+})$ increases from 0.12 to 0.86	<196 ± 12[a]
CD_4–B_4H_{10}–$(CH_3)_2CO$	100:0.71:1.1	0.13–0.46	$B_4H_9^+ + (CH_3)_2CO \rightarrow (CH_3)_2COH^+ + B_4H_8$	Reaction occurs; $I_{(CH_3)_2COH^+}/I_{(CH_3)_2COD^+}$ increases from 0.12 to 0.30	<188 ± 2[b]
CD_4–B_4H_{10}–C_3D_6	100:1.0:1.3	0.3–0.5	$B_4H_9^+ + C_3D_6 \rightarrow C_3D_6H^+ + B_4H_8$	Reaction not observed; signal due to possible $C_3D_6H^+$ species does not increase with P_s	>180 ± 2[c]
CD_4–B_4H_{10}–C_4H_8	100:1.0:1.0	0.45	$B_4H_9^+ + C_4H_8 \rightarrow C_4H_9^+ + B_4H_8$	Reaction not observed: $(I_{C_4H_9^+}/I_{C_4H_8D^+})_s - (I_{C_4H_9^+}/I_{C_4H_8D^+})_b \approx 0$	>174 ± 5[d]
CD_4–B_4H_{10}–C_2H_4	100:0.76:0.82	0.40	$B_4H_9^+ + C_2H_4 \rightarrow C_2H_5^+ + B_4H_8$	Reaction not observed; $I_{C_2H_5^+}/I_{C_2H_4D^+}$ not increased over that observed in blank	>160 ± 2

[a] The large uncertainty in $PA(C_3H_4)$ is due to the fact that the $\Delta H_f(C_3H_5^+)$ is known to only 0.5 eV: F. Dorman, *J. Chem. Phys.*, **43**, 3507 (1965). [b] M. A. Haney and J. L. Franklin, *J. Phys. Chem.*, **73**, 4328 (1969). [c] $PA(C_3D_6)$ based on the assumption that the protonated species is the *sec*-$C_3H_7^+$ ion. [d] PA(1-butene) based on the assumption that the protonated ion is the most stable straight-chain species.

or $PA(B_5H_9) = 167 \pm 6$ kcal/mol, where the uncertainty includes uncertainties in the published data for H_2O and H_2S.[13] The relative ordering of the proton affinities of B_5H_9 with reference compounds in Table IV is $C_3H_6 > C_4H_8 > H_2S > B_5H_9 > H_2O > C_2H_4 > CH_4$.

Observation of proton transfer in gaseous mixtures containing B_6H_{10} shows that this molecule is protonated by $C_3H_7^+$, $C_4H_9^+$, and PH_4^+ (Table VI) and is therefore a stronger base than B_5H_9. In the CI mass spectra of PH_3, PH_4^+ is the predominant ion produced through reaction sequences of the primary ions. Proton transfer from PH_4^+ to B_6H_{10} is inferred from the dramatic increase in $B_6H_{11}^+$ and decrease in PH_4^+ when a small quantity of B_6H_{10} is added to the system. This places the proton affinity of B_6H_{10} above 186 ± 1 kcal/mol. A definitive upper limit on $PA(B_6H_{10})$ was not established by three-component reaction sequences because of limited choices of suitable reference bases with proton affinities between 190 and 200 kcal/mol. However, an estimate of the $PA(B_6H_{10})$ was obtained from the simple relationship

$$(IP + PA)_{B_5H_9} = (IP + PA)_{B_6H_{10}} \qquad (13)$$

where the IP's are ionization potentials of B_5H_9 and B_6H_{10}. This expression is obtained by assuming that the energies to dissociate a hydrogen atom from $B_5H_{10}^+$ and $B_6H_{11}^+$ are equivalent. For molecules like the boron hydrides, which have several B–H bonds and similar structures, this is a reasonable assumption. From published[14] ionization potentials for B_5H_9 and B_6H_{10}, $IP(B_5H_9) - IP(B_6H_{10}) = 28 \pm 2$ kcal/mol. Thus, using $PA(B_5H_9) = 167 \pm 6$ kcal/mol we find $PA(B_6H_{10}) = 195 \pm 8$ kcal/mol. This is above the lower limit obtained from proton-transfer data.

Results of CI studies of three-component gaseous mixtures containing B_4H_{10} are summarized in Table VI. In these systems with CD_4 as carrier gas, the boron hydride spectrum is almost exclusively that of $B_4H_9^+$ (note Figure 2). The tendency for this ion to transfer a proton to a base (R) should be noted through a secondary reaction

$$B_4H_9^+ + R \longrightarrow RH^+ + B_4H_8 \qquad (14)$$

Since B_4H_8 is not a stable species under ordinary conditions, it was not possible to observe the reverse of eq 14. Proton transfer in reaction 14 was postulated if the intensity of RH^+ increased significantly in relation to RD^+ which is produced by the reaction of R with CD_5^+. The data in Table VI indicate the relative ordering of proton affinities

$$C_2H_4 < C_4H_8 < C_3D_6 < B_4H_8 < (CH_3)_2CO$$

This leads to $PA(B_4H_8) = 184 \pm 6$ kcal/mol.

Kinetics of the CH_5^+–B_5H_9 Proton-Transfer Reaction. The exponential decay of CH_5^+ in Figure 3 above the concentration maximum indicates pseudo-first-order kinetics for the reaction of CH_5^+ with B_5H_9. In order to determine the rate constant k for this reaction, we must estimate the residence time τ of the CH_5^+ ions in the ionization chamber. The reactant ions of methane are formed at or near the electron beam and exit at the ion exit slit. If we assume that CH_5^+ makes no collisions in the ion source, we can obtain the free flight residence time, τ_{ff}, from electrostatic considerations

$$\tau_{ff} = (2dm/eE)^{1/2} \qquad (15)$$

where d is the distance from the electron beam to the ion exit slit in centimeters, m is the mass of the CH_5^+ ion, e is the electrostatic charge, and E is the electric field strength in volts/centimeter. Figure 4 contains a semilogarithmic plot of the relative intensity of CH_5^+ *vs.* the pressure of B_5H_9 ($P_{B_5H_9}$) in the ion source. The slope of the least-squares line drawn gives $k\tau$. Using $\tau_{ff} = 1.51 \times 10^{-6}$ sec, we obtain $k_{ff} = 2.7 \times 10^{-8}$ cm^3/(molecule sec). The CH_5^+ ion makes roughly 150 collisions with methane at the highest pressure employed in Figure 3. Therefore, the assumption that there are no collisions, and that τ is independent of the source pressure, is a poor one. In order to obtain a better value for the rate constant, τ must be determined from ion-mobility theory[15–21]

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$$\tau = d/v_d = d/\varkappa E \quad (16)$$

where v_d is the drift velocity in the field direction and $\varkappa$ is the ionic mobility. Langevin's mobility theory predicts that

$$\varkappa = A(1 + M/m)^{1/2}/\sqrt{\rho(K - 1)} \quad (17)$$

where ρ is the gas density, M is the mass of the molecule, m is the mass of the ion, K is the dielectric constant, and A is taken from Hasse's table[16] as a function of a parameter

$$\lambda^2 = 8\pi P D_{12}^4/(K - 1)e^2 \quad (18)$$

where P is the pressure and D_{12} is the sum of the radii of the ion and neutral molecule. Taking D_{12} as 2.82 Å[22] and $P = 0.5$ mm, we obtain $\lambda = {\sim}7 \times 10^{-3}$, $A = 0.5105$, and the Langevin equation becomes

$$\varkappa = \frac{0.5105}{\sqrt{\rho(K - 1)}}\left(1 + \frac{M}{m}\right)^{1/2} \text{ (polarization limit)} \quad (19)$$

This result is identical with the quantum mechanical calculation of the mobility[17,21]

$$\varkappa = \frac{(760)(T)}{(P)(273)}\varkappa_0 = \frac{(760)(T)}{(P)(273)}\frac{35.9}{\sqrt{\alpha Mr}} \text{ cm}^2/(\text{V sec}) \quad (20)$$

where $\varkappa_0$ is the reduced mobility, α is the polarizability of the neutral gas expressed in atomic units (a_0^3), and Mr is the reduced mass measured in proton mass units. Thus we can write for the residence time in seconds

$$\tau = \frac{(d)(\alpha Mr)^{1/2}(273)(200)}{(E)(760)(35.9)(T)} P_{B_5H_9} = CP_{B_5H_9} \quad (21)$$

where C is the constant of proportionality. Using $d = 0.76$ cm, $E = 11.6$ V/cm, $\alpha = 2.56 \times 10^{-24}$ cm^3,[23] $Mr = 8.206$, and $T = 373$°K, we obtain $C = 4.18 \times 10^{-3}$ sec/mm. Thus a semilogarithmic plot of CH_5^+ *vs.* $(P_{B_5H_9})^2$ (shown in Figure 4) will have a slope equal to kC. The slope of the least-squares line drawn is 9.1×10^{-2}, and finally k is estimated to be 1.93×10^{-9} cm^3/(molecule sec).

Discussion

Chemical ionization studies of boron hydrides in methane have shown that B_2H_6, B_4H_{10}, and B_5H_{11} react to form $(M - 1)^+$ ions, and that B_5H_9 and B_6H_{10} react to form $(M + 1)^+$ ions. It appears therefore that boron hydrides which do not form a parent ion by electron impact (B_2H_6, B_4H_{10}, and B_5H_{11}) also do not form a stable protonated species. From thermochemical data available for $B_2H_5^+$ and B_2H_6 we have for eq 22 the following ΔH. This calculation, which is

$$B_2H_6 + H^+ \longrightarrow B_2H_5^+ + H_2 \quad (22)$$

$$\Delta H = -143.5 \text{ kcal/mol}$$

based on data for vertical ionization for B_2H_6 (11.9 eV from electron impact[14] and 11.9 eV from photoelectron studies[24]) is probably a few kilocalories per mole too positive. Since $B_2H_7^+$ is not observed by CI, we can assume that the hypothetical process $B_2H_7^+ \rightarrow B_2H_5^+ + H_2$ is exothermic. Thus the ΔH for reaction 22 indicates that the proton affinity of B_2H_6 is roughly less than 143.5 kcal/mol. Extending eq 13 to include other boron hydrides, we calculate using adiabatic IP(B_2H_6) = 11.4 eV[24] and B_5H_9 for reference, PA(B_2H_6) = 145 kcal/mol. This calculation indicates that B_2H_6 is a stronger base than CH_4 (PA(CH_4) = 127 kcal/mol), but the absence of a $(M + 1)^+$ ion in the CI mass spectrum of B_2H_6 in methane shows that dissociative proton transfer predominates over simple proton transfer.

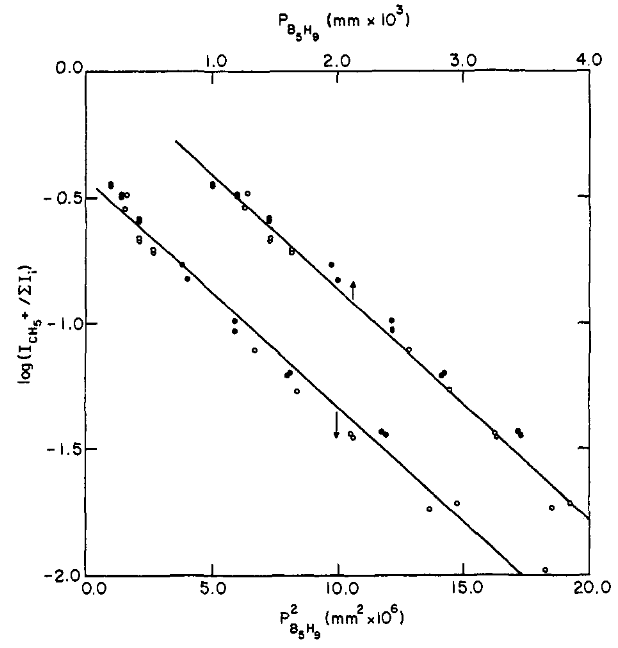

Figure 4. Semilog plots of $I_{CH_5^+}/\Sigma I_i$ *vs.* $P_{B_5H_9}$ (upper) and $P^2_{B_5H_9}$ (lower). Data obtained from sample of composition CH_4:B_5H_9 = 200:1.

Adiabatic ionization potentials for B_4H_{10} and B_5H_{11} are not available for estimation of their proton affinities by eq 13.

In addition to acting as proton acceptors, B_5H_9 and B_6H_{10} react with hydrocarbon ions to form complexes that may be categorized into isoelectronic pairs (C_3H_7-$B_5H_7^+$-$C_2H_5B_6H_{10}^+$, etc.). The ion $B_5H_{10}^+$ is the major boron hydride ion formed by CI of B_5H_9 and B_5H_{11}. A value of ΔH for the reaction

$$B_5H_{11} + H^+ \longrightarrow B_5H_{10}^+ + H_2 \quad (23)$$

is obtained by combining the proton affinity of B_5H_9 with the ΔH for the dissociation of B_5H_{11} into B_5H_9 and H_2 (−7.2 kcal/mol).[10] Thus for reaction 23, $\Delta H = -174$ kcal/mol. This places a rough upper limit on the proton affinity of B_5H_{11}. We summarize in Table VII measured and estimated values of the proton affinities for some boron hydride molecules.

Table VII. Proton Affinities of Some Boron Hydride Molecules

Molecule	PA, eV
B_2H_6	≤6.3
B_4H_8	7.98 ± 0.26
B_5H_9	7.24 ± 0.26
B_5H_{11}	≤7.5
B_6H_{10}	8.46 ± 0.35

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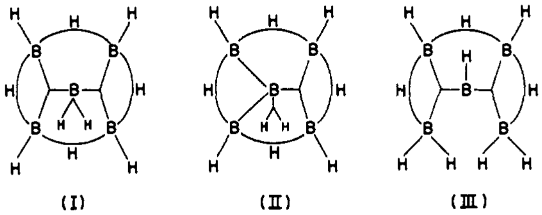

(I) (II) (III)

Figure 5. Possible structures for $B_5H_{10}^+$.

Prediction of a C_2 or C_{2v} structure for $B_5H_{10}^+$ is based on the following arguments. Theoretical calculations[25] for B_5H_9 indicate that the apical boron atom (B_1) has a higher electron density than a boron atom in the base plane of the polyhedron. Thus, attack of B_5H_9 by CH_5^+ should lead to attachment of a proton at the B_1 site. From Lipscomb's[26] STYX bonding descriptions, a possible structure for $B_5H_{10}^+$ is designated 4201, a species with four H bridges, two three-center framework bonds, no single B–B bonds, and one additional terminal H at B_1 (structure I in Figure 5). However, an undesirable feature of the 4201 structure for $B_5H_{10}^+$ is that the effect of protonation of B_5H_9 would then be to increase the extent of terminal bonding but only at the expense of a decreased stability of the polyhedral framework. An alternate orbital description of $B_5H_{10}^+$ that should also lead to a configuration with a twofold axis is structure II in Figure 5. In this model, the framework bonding in the B_5H_9 polyhedron is retained and an H^+ is added at B_1 to form a three center

$$\underset{\text{B}}{\text{H—H}}$$

bond constructed from two s orbitals on H atoms and a p boron orbital extended along the symmetry axis. There now appears some precedent for this type of bonding in CH_5^+. Theoretical calculations[27] indicate that a C_s structure for CH_5^+ is more stable than the D_{3h} or C_{4v} configuration. The calculated C_s structure for CH_5^+ has three approximately normal C–H bonds with bond lengths of 1.14 Å and bond angles of 110°. However, the other two C–H bonds have long bond lengths of 1.21 Å and form an HCH bond angle of only 50°. This results in one short H–H bond distance of about 1.02 Å, which is comparable to that on H_2^+ (1.06 Å),[28] and indicates some degree of H–H bonding. The ion $B_5H_{10}^+$ produced by chemical ionization of B_5H_{11} is probably formed by hydride ion abstraction at the B_1 site, since this is the β atom with the highest electron density.[25] This suggests a possible 3202 structure for $B_5H_{10}^+$ (III in Figure 5). However, it seems quite doubtful that an open structure of this type would not undergo rearrangement with stabilization through an additional H bridge as in I or II.

For $B_6H_{11}^+$, possible structures include that with a three-center terminal bond at the apical B atom and one in which the added proton assumes the fifth bridge position to give a species with C_{5v} configuration. The high proton affinity of B_6H_{10} suggests that $B_6H_{11}^+$ may be a sufficiently stable cation to exist in solution or in the crystalline state.

Acknowledgments. We are grateful for support of the Army Research Office, Durham, N. C., and the Advanced Research Projects Agency through the Materials Science Center at Cornell University. We appreciate the assistance of Dr. F. Scholer, and Dr. E. R. Lory in preparing samples of boron hydrides used in this study.

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