may be used with either (6) or (7) to obtain $k_3 = (3.4 \pm 1.2) \times 10^{-10}$ cm^3 molecule^{-1} sec^{-1}.

Conclusions

Ferrocene is amenable to study in the ion source of a mass spectrometer at pressures up to 1.5×10^{-2} Torr. The fragment ions Fe^+ and $FeC_5H_5^+$ both undergo rapid charge transfer with neutral ferrocene. These reactions are exothermic for ground-state reactants.

The binuclear adduct $Fe_2(C_5H_5)_3^+$ is formed from reaction of $FeC_5H_5^+$ and ferrocene and does not undergo further reaction under the present conditions. Charge transfer involving $FeC_5H_5^+$ occurs about six times as fast as the competing adduct formation. The rate constants for reaction of Fe^+ and $FeC_5H_5^+$ with ferrocene are about twice those predicted by the polarization theory of Gioumousis and Stevenson,[17] using the relationship

$$k = 2\pi e\sqrt{\alpha/\mu} \qquad (8)$$

where e is the charge on the ion, α is the molecular polarizability of ferrocene,[9] and μ is the reduced mass of the reacting system. Considering the limitations of the theory,[18] the agreement is good and perhaps fortuitous, but it suggests no significant steric or energetic barrier to these reactions.

Further studies of gaseous ion chemistry of metal complexes should provide useful information about reactions and chemical species not occurring or not easily studied in condensed or neutral systems.

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

[17] G. Gioumousis and D. P. Stevenson, *J. Chem. Phys.*, **29**, 294 (1958).

[18] L. Friedman, *Annu. Rev. Phys. Chem.*, **19**, 273 (1968).

Low-Temperature Chemical Ionization Mass Spectrometry of Boron Hydrides. The Proton Affinities of Diborane and Tetraborane(10)

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Abstract: Low-temperature chemical ionization spectra of B_2H_6, B_4H_{10}, and B_5H_9 in methane have been obtained. Protonation of B_2H_6 to yield $B_2H_7^+$ is observed in CH_4 between 79 and 86°K. The proton affinity of B_2H_6 is determined to be 147 ± 4 kcal/mol. In the B_2H_6–CH_4 and B_2H_6–H_2 systems $B_4H_{11}^+$ is formed by addition of $B_2H_5^+$ to B_2H_6 between 80 and 140°K and between 80 and 115°K, respectively. From the observed heat of formation of $B_4H_{11}^+$, the proton affinity of B_4H_{10} is calculated to be 144 ± 5 kcal/mol. For the B_4H_{10}–CH_4 and B_5H_9–CH_4 systems ion interconversions are studied as a function of temperature. These results indicate the relative ordering of the zero point energies of several $B_4H_n^+$ and $B_5H_n^+$ ions.

In a recent publication[1] we reported the results of a chemical ionization study of the common boron hydrides with a number of ionizing reagents. These results showed that B_5H_9 and B_6H_{10} are moderately strong bases. Independently, Johnson, *et al.*,[2] have isolated the $B_6H_{11}^+$ cation in a strong acid medium. Chemical ionization of B_2H_6, B_4H_{10}, and B_5H_{11} by CH_5^+ at source temperatures of 100–200° leads to hydride abstraction from the boron hydride with the formation of $(M - 1)^+$ ions. Only an estimate of the proton affinity of diborane could be obtained from these measurements. It is possible that failure to detect the $(M + 1)^+$ ion in these experiments was due to thermodynamic instability of the ion at the operating source temperature or to complicated kinetic factors in the proton transfer mechanism. To examine these problems further we have modified our experimental technique for study of these processes at low temperatures. The results of this investigation have led to a better understanding of the nature of the proton transfer process in these systems and have provided information on the proton affinities of B_2H_6 and B_4H_{10}.

Experimental Section

The design of the low-temperature chemical ionization (CI) source used in this study is illustrated in Figure 1. The ion box and inlet tube were constructed of 304 stainless steel. Source pressures were measured with a McLeod gauge through a side-arm connection into the source cavity. An ion repeller was located 1.2 cm from the ion exit hole. For most experiments the source field strength was maintained at either 10 or 23 V/cm (in this range of field strengths the extent of chemical ionization was seen to vary but not the essential processes of interest). Rhenium filaments were used, and the electron accelerating energy was fixed at 300 V. The source was sandwiched between two heavy copper blocks fitted with refrigeration coils. With liquid nitrogen as coolant it was possible to attain source temperatures between 79 and 310°K (the ambient temperature with hot filament). Temperatures were measured with a chromel–alumel thermocouple spot-welded to the source. The thermocouple voltage was monitored continuously on a Varian Model No. G-2010 recorder. The source pressure was controlled by adjusting the inlet gas flow rate with a Nupro

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[1] J. Solomon and R. F. Porter, *J. Amer. Chem. Soc.*, **94**, 1443 (1972).

[2] H. D. Johnson, II, V. T. Brice, G. L. Brubaker, and S. G. Shore, *J. Amer. Chem. Soc.*, **94**, 6711 (1972).

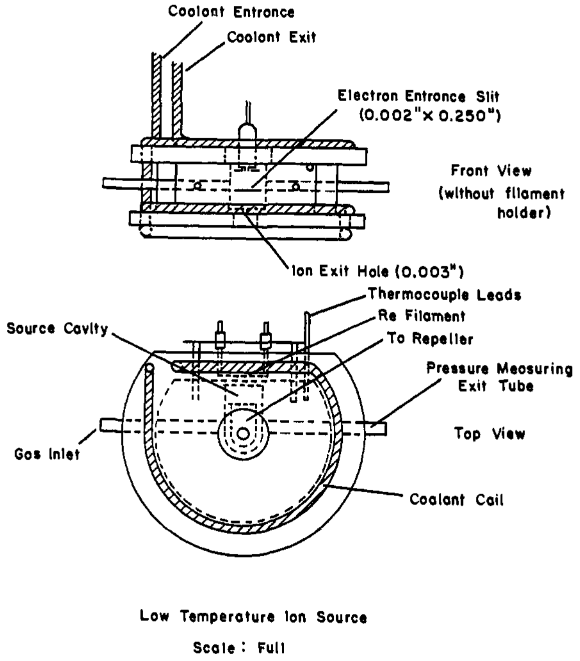

Figure 1. Low-temperature chemical ionization ion source.

Model No. SS-4M needle valve. The establishment of temperature equilibrium between the gases and the walls of the ionization chamber in this type of source has been considered by Beggs and Field.[3] The arguments presented in their paper are generally applicable to the work described here.

The mass analyzer was assembled from an Extranuclear Model 270–9 quadrupole mass filter and a particle detector consisting of a 24-stage Mg-Al electron multiplier located on axis with the quadrupole. The vacuum housing was mounted to a 4-in. diffusion pump equipped with a 4-in. "Cryosorb" (Granville Phillips) stainless steel baffle. Residual pressure in the quadrupole region reached about 10^{-4} mm when the source pressure of CH_4 was 0.80 mm. One operational advantage of the quadrupole configuration is the low ion accelerating voltage required (between 5 and 10 V).

In studies of methane–boron hydride mixtures some experimental restrictions are imposed by the properties of the boron compound. For B_4H_{10} mixtures the lowest operating temperature was about 140°K due to condensation of B_4H_{10} on the walls of the source. A problem that is frequently encountered in chemical ionization of methane–boron hydride mixtures is a notable decrease in operational sensitivity from that experienced with pure hydrocarbon gases. This effect is apparently due to the formation of solid deposits on the exterior surface of the source as the gases exit from the slit aligned with the hot filament.

All hydrocarbon gases (except CD_4) used in these experiments were Matheson reagent grade. Methane-d_4 (minimum isotopic purity of 99 atom % D) was supplied by Merck Sharp and Dohme. The boron hydrides, B_2H_6,[4] B_2D_6,[4] and B_4H_{10},[5] were prepared by standard literature procedures. Pentaborane(9) was obtained from the Callery Chemical Co. Purity of the boron hydrides was checked by infrared and mass spectra and by glpc. Sample mixtures of hydrocarbon–boron hydride were prepared by transfer of an appropriate quantity of hydrocarbon to a bulb containing a known pressure of boron hydride.

B_5H_9–CH_4 System. Chemical ionization of B_5H_9 in methane yields $B_5H_{10}^+$ as the major product at source pressures of the order of 0.5 mm. At low source pressures of the order of 0.05 mm, fragmentation processes leading to $B_5H_8^+$ and $B_5H_6^+$ become important. For a source pressure of 0.06 mm and a gas composition $B_5H_9:CH_4 = 1:200$ the ratio $\Sigma I_{(B_5H_n^+)}/\Sigma I_i$ was constant with the limits 0.40 ± 0.05 over a temperature range 200–300°K. This showed that the total extent of the chemical ionization reaction was insensitive to temperature. However, a dramatic increase in $I_{(B_5H_{10}^+)}/\Sigma I_{(B_5H_n^+)}$ with decreasing temperature was noted as shown by the intensity profiles in Figure 2. Also shown in Figure 2 is a breakdown of the intensities of deuterium labeled products observed in studies of a B_5H_9–CD_4 mixture. The H–D isotope distributions in the ion products resulting from loss of one or two hydrogen molecules from $B_5H_9D^+$ for several temperatures are given in Table I. Based on a simple reaction sequence (eq 1) it is evident from the results

$$\begin{tikzcd} & B_5H_8^+ \arrow[r, "-H_2"] & B_5H_6^+ \\ B_5H_9D^+ \arrow[ur, "-HD"] \arrow[dr, "-H_2"'] & & \\ & B_5H_7D^+ \arrow[uur, "-HD"] \arrow[r, "-H_2"'] & B_5H_5D^+ \end{tikzcd} \qquad (1)$$

that the fragmentation processes are close to statistical in the dis-

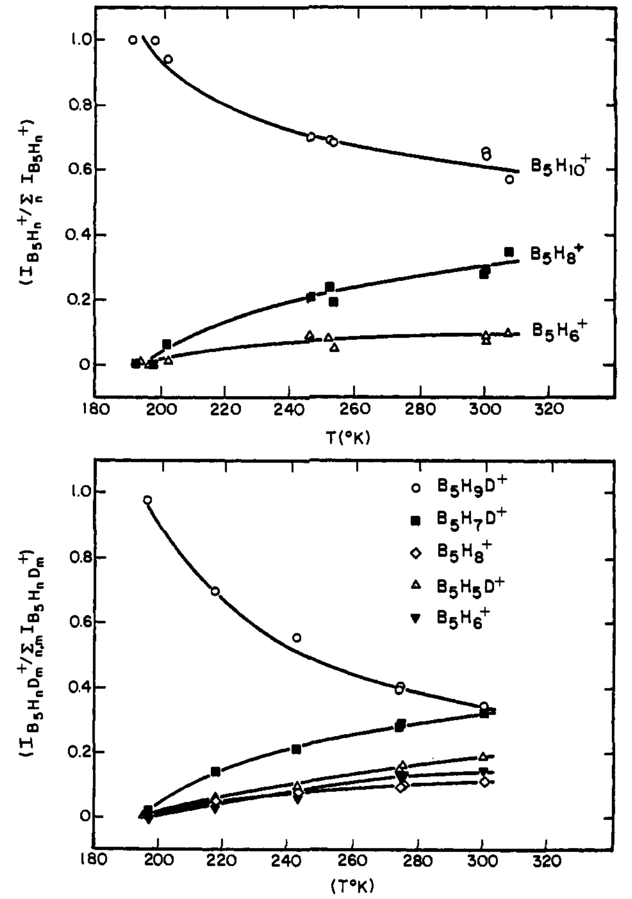

Figure 2. Temperature dependence for the $B_5H_n^+$ ions: source pressure (P_s = 0.07 mm); sample composition, $CH_4:B_5H_9$ = 200:1. Temperature dependence for the $B_5H_nD_m^+$ ions: source pressure (P_s = 0.06 mm); sample composition, $CD_4:B_5H_9$ = 100:1.

Table I. Isotopic Composition of Ions from the Decomposition of $B_5H_9D^+$ Produced by CI of B_5H_9 in CD_4[a]

T, °K	$I_{B_5H_7D^+}/I_{B_5H_8^+}$	$I_{B_5H_5D^+}/I_{B_5H_6^+}$
300	2.8	1.4
273	3.1	1.2
273	3.5	1.3
242	2.9	1.7
217	2.8	2.0
Av ratio (obsd)	$3.0^{+0.5}_{-0.2}$	$1.5^{+0.5}_{-0.3}$
Statistical ratio (calcd)	4.0	1.5

[a] P_s = 0.06 mm and $B_5H_9:CD_4$ = 1:100.

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(3) D. D. Beggs and F. H. Field, *J. Amer. Chem. Soc.*, 93, 1567 (1971).

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

(5) M. J. Klein, B. D. Harrison, and I. J. Solomon, *J. Amer. Chem. Soc.*, 80, 4149 (1958).

tribution of the D atom. A process involving deuteron transfer to B_5H_9 and rapid elimination of an HD molecule at one site in the molecule would be expected to lead only to totally hydrogenated product. Results of the temperature-dependence studies and the isotope distribution experiments lead to a fragmentation mechanism involving a common activated intermediate. We propose the following scheme

$$CH_5^+ + B_5H_9 \xrightarrow{k_1} (B_5H_{10}^+)^* + CH_4 \quad \text{(rate determining)} \tag{2}$$

$$(B_5H_{10}^+)^* \xrightarrow{k_2} B_5H_8^+ + H_2 \quad \text{(activated decomposition)} \tag{3}$$

$$(B_5H_{10}^+)^* + CH_4 \xrightarrow{k_3} B_5H_{10}^+ + CH_4 \quad \text{(quenching)} \tag{4}$$

$$(B_5H_{10}^+) \xrightarrow{k_4} B_5H_8^+ + H_2 \quad \text{(thermal decomposition)} \tag{5}$$

Using the normal steady-state assumption for the activated intermediate we have for the hypothetical intensity of $(B_5H_{10}^+)^*$

$$I_{(B_5H_{10}^+)^*} = k_1 P_{B_5H_9} I_{(CH_5^+)}/(k_2 + k_3 P_{CH_4}) \tag{6}$$

The primary reaction is known to be exothermic to the extent of about 42 kcal/mol and a fraction of this will result in excitation of the activated complex $(B_5H_{10}^+)^*$. The collision frequency for a $(B_5H_{10}^+)^*$ species with CH_4 is estimated to be of the order of 10^7/sec at a source pressure of 0.1 mm. Thus the lifetime of the activated species in the absence of collisions is of the order of 10^{-7} sec. The residence time of an ion in the source is about 10^{-5} sec so the quenching step must be relatively rapid at moderately high pressures. The observed ratio $I_{(B_5H_8^+)}/I_{(B_5H_{10}^+)}$ is then a measure of the relative rates of decomposition (reaction path 3) and stabilization (reaction path 4) of $B_5H_{10}^+$.

$$\frac{I_{(B_5H_8^+)}}{I_{(B_5H_{10}^+)}} = \frac{k_2 I_{(B_5H_{10}^+)^*} + k_4 I_{(B_5H_{10}^+)}}{k_3 P_{CH_4} I_{(B_5H_{10}^+)^*} - k_4 I_{(B_5H_{10}^+)}} \tag{7}$$

Since $B_5H_{10}^+$ is thermally stable at a source pressure of 0.5 mm and temperature of 100°, we can assume that reaction 4 is relatively unimportant and that k_4 is less than $1/\tau_{res}$. This leads to a simple approximation

$$I_{(B_5H_8^+)}/I_{(B_5H_{10}^+)} = k_2/k_3 P_{CH_4} \tag{8}$$

The slope of the reciprocal temperature dependence in log $I_{(B_5H_8^+)}/I_{(B_5H_{10}^+)}$ is then taken as the difference in activation energy between reaction 3 and 4 (see Figure 3).

It is anticipated that k_2 will be insensitive to temperature, and that the temperature dependence of ion intensities reveals mainly the effect due to quenching or stabilization of $B_5H_{10}^+$. At very high quenching rates (high pressures) the thermal decomposition of $B_5H_{10}^+$ measured by k_4 should become the rate-determining process leading to $B_5H_8^+$.[6]

B_2D_6-$CH_4(CD_4)$ and B_2H_6-H_2 Systems. In Tables II and III chemical ionization mass spectra of diborane in methane and in hydrogen at low temperature are given. The major differences in these spectra from those recorded at ambient source temperature are the appearance of $B_2D_6H^+$ $(B_2D_7^+)$ (subsequently referred to as "$B_2H_7^+$") over a short temperature interval near 80°K and the appearance of $B_4D_{11}^+$ $(B_4H_{11}^+)$ over a temperature range between 80 and 140°K.

Table II. Chemical Ionization Mass Spectrum of B_2D_6 in Methane at 82°K[a]

Ion	Rel intensity $I_i/\Sigma_i I_i$	Ion	Rel intensity $I_i/\Sigma_i I_i$
CH_5^+	0.0151	$B_2D_6H^+$	0.0064
$C_2H_4^+$	0.0093	$C_3H_5^+$	0.0382
$C_2H_5^+$	0.228	$C_3H_7^+$	0.0209
$C_2H_7^+$	0.0022	$C_2H_9^+$	0.0838
$B_2D_5^+$	0.295	$C_3H_{13}^+$	0.0547
$C_2H_9^+$	0.165	$C_4H_9^+$	0.0038
		$B_4D_{11}^+$	0.0774

[a] Source pressure = 0.22 mm; gas composition $B_2D_6:CH_4$ = 1:1000.

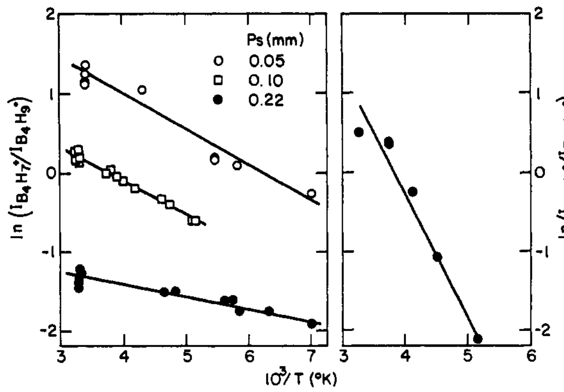

Figure 3. Semilog plots of $I_{(B_4H_7^+)}/I_{(B_4H_9^+)}$ and $I_{(B_5H_8^+)}/I_{(B_5H_{10}^+)}$ *vs.* $10^3/T$; sample compositions, $CH_4:B_4H_{10}$ = 200:1 and $CH_4:B_5H_9$ = 200:1 (P_s = 0.06 mm), respectively.

Table III. Chemical Ionization Mass Spectrum of B_2H_6 in Hydrogen at 83°K[a]

Ion	Rel intensity $I_i/\Sigma_i I_i$	Ion	Rel intensity $I_i/\Sigma_i I_i$
H_2^+	0.0230	N_2H^+	0.0034
H_3^+	0.6830	$B_3H_6^+$	0.0009
H_5^+	0.0950	$B_4H_8^+$	0.0048
BH_2^+	0.0075	$B_4H_{10}^+$	0.0008
$B_2H_5^+$	0.1700	$B_4H_{11}^+$	0.0120

[a] Source pressure = 0.22 mm; gas composition $B_2H_6:H_2$ = 1:2000.

B_4H_{10}-CH_4 System. Chemical ionization mass spectra of B_4H_{10} in methane were obtained over a temperature range 140–300°K. A complete spectrum for one set of conditions is given in Table IV. The main products containing boron are $B_4H_7^+$ and $B_4H_9^+$. A species, $B_4H_{11}^+$, of low intensity is also observed. This ion was not observed in CI experiments at conventional source temperatures (~100°). For a fixed source pressure of 0.05 mm and a $B_4H_{10}:CH_4$ composition of 1:200 the fraction of $B_4H_n^+$ ions in the spectrum, as indicated by $\Sigma I_{(B_4H_n^+)}/\Sigma I_i$, was constant within the limits 0.21 ± 0.02 over a temperature range 170–250°K. However, a marked change was noted in the relative intensities of $B_4H_9^+$ and $B_4H_7^+$ with $I_{(B_4H_9^+)}/\Sigma I_{(B_4H_n^+)}$ increasing as the source temperature was decreased. The effects of temperature and pressure on the intensity distribution are shown in Figure 4. The temperature-dependence data for ions in the B_4H_{10} and B_5H_9 system are qualitatively similar. By analogy with the B_5H_9 system we propose the following mechanism for CI of B_4H_{10}

$$B_4H_{10} + CH_5^+ \xrightarrow{k_1} (B_4H_{11}^+)^* + CH_4 \quad \text{(rate determining)} \tag{9}$$

$$(B_4H_{11}^+)^* \xrightarrow{k_2} (B_4H_9^+)^* + H_2 \quad \text{(fast)} \tag{10}$$

$$(B_4H_{11}^+)^* + CH_4 \xrightarrow{k_3} B_4H_{11}^+ + CH_4 \quad \text{(quenching)} \tag{11}$$

$$(B_4H_9^+)^* \xrightarrow{k_4} B_4H_7^+ + H_2 \quad \text{(activated decomposition)} \tag{12}$$

$$(B_4H_9^+)^* + CH_4 \xrightarrow{k_5} B_4H_9^+ + CH_4 \quad \text{(quenching)} \tag{13}$$

$$B_4H_9^+ \xrightarrow{k_6} B_4H_7^+ + H_2 \quad \text{(thermal decomposition)} \tag{14}$$

Experiments with B_4H_{10}-CD_4 mixtures have shown that the CI products do not contain deuterium. This indicates that the activated intermediate $(B_4H_{11}^+)^*$ probably has a very short lifetime. Subsequent results from CH_4-B_2H_6 studies show that an ion $B_4H_{11}^+$ is stabilized at temperatures below 140°K. Temperature-dependence data (Figure 4) reflect mainly the effect of competition between reactions 12 and 13. Apparent activation energies for

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[6] S. A. Fridmann and R. F. Porter, Abstracts, 20th Annual Conference on Mass Spectrometry and Allied Topics, Dallas, Tex., June 1972, p 325.

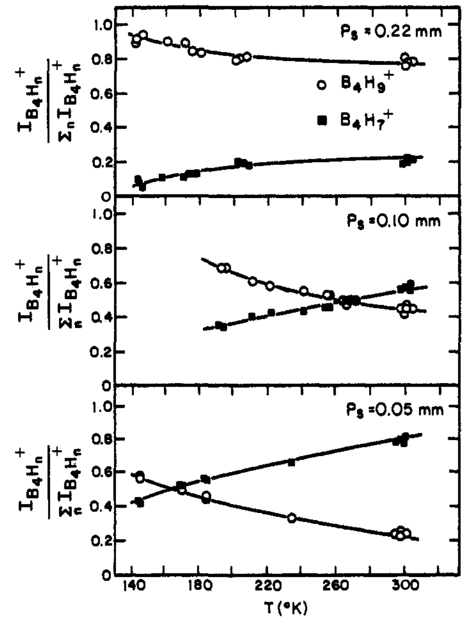

Figure 4. Temperature dependence for the $B_4H_n^+$ ions at three source pressures, sample compositions, $CH_4:B_4H_{10}$ = 200:1.

Table IV. Chemical Ionization Mass Spectrum of B_4H_{10} in Methane at 203 °K[a]

Ion	Rel intensity I_i/Σ_iI_i	Ion	Rel intensity I_i/Σ_iI_i
CH_5^+	0.0515	$C_3H_5^+$	0.0176
$C_2H_3^+$	0.1670	$B_4H_7^+$	0.1440
$C_2H_4^+$	0.0164	$B_4H_9^+$	0.0960
$C_2H_5^+$	0.5030	$B_4H_{11}^+$	0.0032

[a] Source pressure = 0.05 mm; gas composition $B_4H_{10}:CH_4$ = 1:200.

quenching are given in Table V. These data show that on a zero point energy scale $B_4H_9^+$ lies below $B_4H_7^+ + H_2$.

Table V. Temperature-Dependence Data for Boron Hydride Ions Formed by Chemical Ionization

System	Composition	P, mm	Effective process	$-\Delta E$ (stabilization), kcal/mol
$B_4H_{10}:CH_4$	1:200	0.05		0.90
$B_4H_{10}:CH_4$	1:200	0.10	$(B_4H_9^+)^* \longrightarrow B_4H_9^+$	0.85
$B_4H_{10}:CH_4$	1:200	0.22		0.34
$B_5H_9:CH_4$	1:100	0.06	$(B_5H_{10}^+)^* \longrightarrow B_5H_{10}^+$	3.2
$B_2H_6:CH_4$	1:1000	0.13	$(B_4H_{11}^+)^* \longrightarrow B_4H_{11}^+$	1.3
$B_2D_6:CH_4$	1:1000	0.10	$(B_2D_6H^+)^* \longrightarrow B_2D_6H^+$	3.4

Proton Affinities of B_2H_6 and B_4H_{10}

A limit on the proton affinities of B_2H_6 and B_4H_{10} may be obtained if the chemical process leading to formation of their protonated species is defined. At low methane pressures the intensity of $B_2H_7^+$ increases approximately as the fourth power of the source pressure (see Figures 5 and 6). This is about one unit higher than that observed for the formation of $C_2H_9^+$ (see also Figure 5), measured under equivalent source conditions. At low source pressures the system is not saturated with respect to CH_4^+ formed in the primary ionization process. Thus the high kinetic order for the formation of $B_2H_7^+$ can be interpreted by postulating the consecutive steps $CH_4^+ \rightarrow CH_5^+ \rightarrow C_2H_9^+$ followed by reaction of $C_2H_9^+$ with B_2H_6. These observations exclude CH_5^+ and $C_2H_5^+$ as the principal reactants with B_2H_6 leading directly to $B_2H_7^+$. At normal source temperature $B_2H_5^+$ is formed mainly by reaction of CH_5^+ with B_2H_6. Chemical ionization experiments with C_2H_6–B_2H_6 mixtures, in which CH_5^+ is not present as a reactant, show that a hydride abstraction reaction between $C_2H_5^+$ and B_2H_6 is of minor importance at pressures below 0.2 mm, although this reaction is thermodynamically favorable. It was found that for a fixed source pressure and temperature, the ratio of $B_2H_5^+$–$B_2H_7^+$ decreased as the gas composition ratio of CH_4–B_2H_6 was increased. This effect, measured over a wide range of composition, is illustrated in Figure 7. To explain the variation in the relative intensities of $B_2H_5^+$ and $B_2H_7^+$ and the pressure-dependence data described

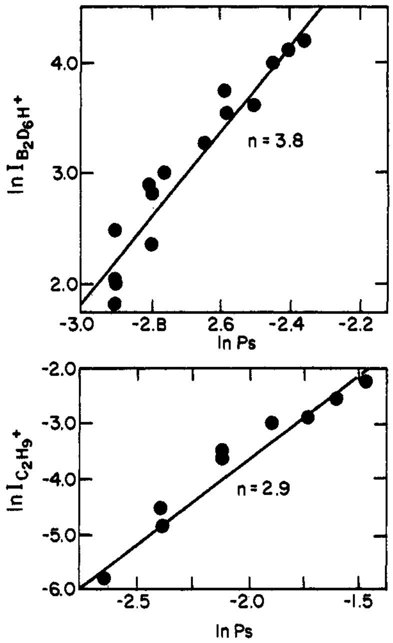

Figure 5. Log–log plots of the normalized $I_{(B_2D_6H^+)}$ and $I_{(C_2H_9^+)}$ vs. P_s at 82 °K; sample composition, $CH_4:B_2D_6$ = 1000:1.

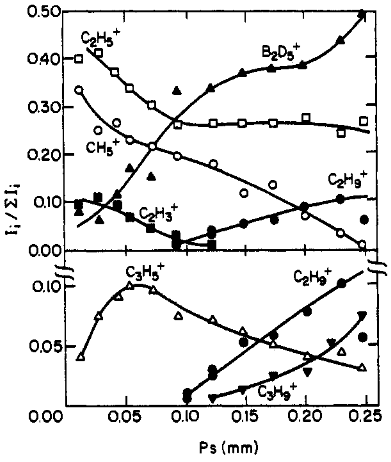

Figure 6. Effect of source pressure on the relative intensity of major ions in the CI spectra of B_2D_6 in CH_4 at 82 °K ($B_2D_6H^+$ and $B_4D_{11}^+$ excluded), sample composition, $CH_4:B_2D_6$ = 1000:1.

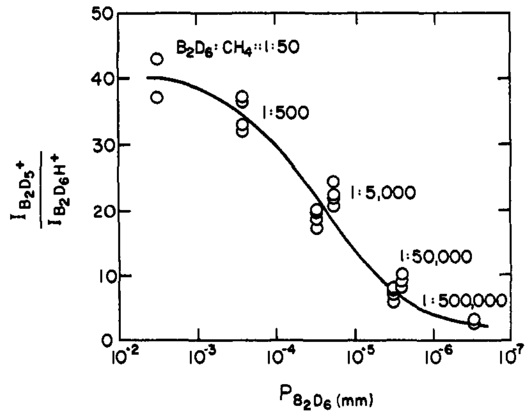

Figure 7. Plot of the $I_{(B_2D_5^+)}/I_{(B_2D_6H^+)}$ *vs.* $P_{B_2D_6}$ at 82°K for varying compositions of B_2D_6 in CH_4.

above the following mechanisms are proposed

$$CH_5^+ + B_2H_6 \xrightarrow{k_1} CH_4 + B_2H_5^+ + H_2 \quad \text{(rate determining)} \quad (15)$$

$$C_2H_9^+ + B_2H_6 \xrightarrow{k_2} 2CH_4 + B_2H_7^+ \quad \text{(rate determining)} \quad (16)$$

$$CH_5^+ + CH_4 \xrightarrow{k_3} C_2H_9^+ \quad \text{(formation)} \quad (17)$$

$$C_2H_9^+ \xrightarrow{k_4} CH_5^+ + CH_4 \quad \text{(decomposition)} \quad (18)$$

Applying the steady-state approximation with respect to $C_2H_9^+$ we find

$$[I_{(C_2H_9^+)}]_{ss} = k_3P_{CH_4}I_{(CH_5^+)}/(k_4 + k_2P_{B_2H_6}) \quad (19)$$

Comparing the rates of formation of $B_2H_5^+$ and $B_2H_7^+$ we then obtain

$$dI_{(B_2H_5^+)}/dI_{(B_2H_7^+)} = k_1(k_4 + k_2P_{B_2H_6})dt_1/k_2k_3P_{CH_4}dt_2 \quad (20)$$

The pressure dependence of B_2H_6 is here explicit. Higher partial pressures of B_2H_6 clearly favor $B_2H_5^+$ production over $B_2H_7^+$. In the limit of very low B_2H_6 concentrations (*i.e.*, small per cent of reaction) the original differential expression for reactions 15 and 16 may be integrated to yield the ratio

$$I_{(B_2H_5^+)}/I_{(B_2H_7^+)} = k_1I_{(CH_5^+)}/k_2I_{(C_2H_9^+)} \text{ for } t = \tau_{res} \quad (21)$$

Hence for a very dilute mixture of B_2H_6 in CH_4 we may approximate the ratio of k_1 to k_2 from our measured spectra. For a mixture with $B_2D_6:CH_4$ = 1:500,000 at a source pressure of 0.20 mm and source temperature of 82°K, $I_{(B_2H_5^+)}/I_{(B_2H_7^+)} = 2.5$ when $I_{(CH_5^+)}/I_{(C_2H_9^+)} = 1.6$. This leads to $k_1/k_2 = 1.6$.

The occurrence of reaction 16 implies that the proton affinity of B_2H_6 is greater than the sum of proton affinity of methane (127 kcal/mol) and the heat of dissociation of $C_2H_9^+$ into CH_4 and CH_5^+ (ΔH = 4.14 kcal/mol)[7] or PA(B_2H_6) is $\geq$131 kcal/mol. The stabilization of $B_2H_7^+$ through reaction 16 may be a result of the dissipation of excess energy in the three molecules of product. It is interesting to note that the hypothetical reaction

$$CH_5^+ + B_2H_6 \longrightarrow B_2H_7^+ + CH_4 \quad (22)$$

is also thermodynamically favorable and should release an energy 4.1 kcal in excess of that for reaction 16. If $B_2H_7^+$ is formed in the primary set of reactions (15),

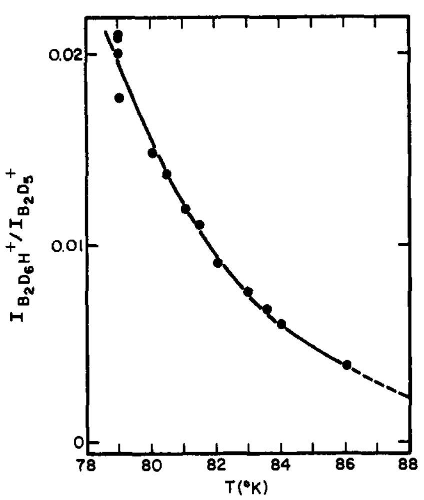

Figure 8. Temperature dependence of the $B_2D_6H^+$ ion intensity at P_s = 0.10 mm, sample composition, $CH_4:B_2D_6$ = 1000:1.

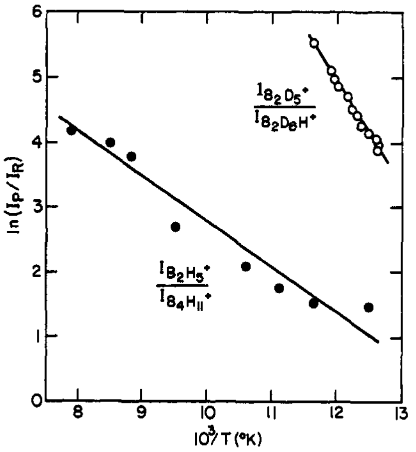

Figure 9. Semilog plots of $I_{(B_2D_5^+)}/I_{(B_2D_6H^+)}$ and $I_{(B_2H_5^+)}/I_{(B_4H_{11}^+)}$ *vs.* $10^3/T$; sample compositions, $CH_4:B_2D_6$ = 1000:1 (P_s = 0.10 mm) and $CH_4:B_2H_6$ = 1000:1 (P_s = 0.13 mm), respectively.

it is apparent that the excess energy is quickly dissipated in the formation of the decomposition products ($B_2H_5^+$ + H_2) (B_2H_6 in CD_4 produces no $B_2H_4D^+$). The temperature dependence of the $B_2H_7^+$ intensity could be obtained only over a very narrow temperature range (see Figure 8). The data as plotted reflect mainly a change in $B_2H_7^+$ concentration rather than those for $B_2H_5^+$ and $C_2H_9^+$ since the latter ions were present in high concentration and were relatively insensitive to temperature over the short range of observation. The apparent activation energy (−3.4 kcal/mol) derived from these data (see Figure 9) most probably reflects the stabilization of $B_2H_7^+$ with respect to $B_2H_5^+ + H_2$. These observations indicate that in zero point energies $B_2H_7^+$ is slightly lower than $B_2H_5^+ + H_2$. Taking a value of 3.0 ± 3.0 kcal/mol as reasonable limits for the heat of dissociation of $B_2H_7^+$ into $B_2H_5^+ + H_2$, we then obtain from the heats of formation of $B_2H_5^+$ (232 kcal/mol),[8] B_2H_6 (9.8 kcal/mol),[9] and H^+ (366 kcal/mol)[8] a value of $\Delta H = -147 \pm 4$ kcal/mol for the reaction

$$H^+ + B_2H_6 \longrightarrow B_2H_7^+ \quad (23)$$

The proton affinity of B_2H_6 is then 6.35 ± 0.20 eV.

The formation of $B_4H_{11}^+$ in CI experiments with H_2–

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(7) F. H. Field and D. P. Beggs, *J. Amer. Chem. Soc.*, 93, 1585 (1971).

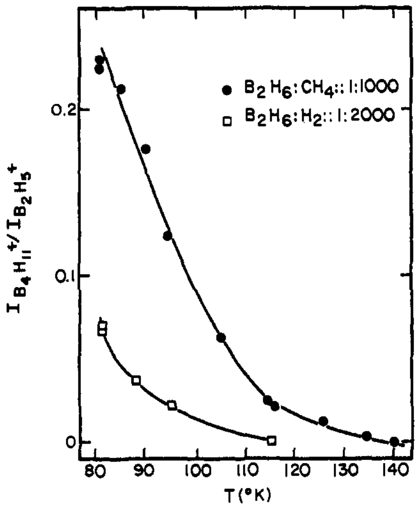

Figure 10. Temperature dependence of the $B_4H_{11}^+$ ion intensity at $P_s(CH_4) = 0.13$ and $P_s(H_2) = 0.22$ mm.

B_2H_6 and CH_4–B_2H_6 mixtures (see Figure 10) may be accounted for by the simple addition reaction

$$B_2H_5^+ + B_2H_6 \longrightarrow (B_4H_{11}^+)^* \xrightarrow[CH_4 \text{ or } H_2]{\text{in}} B_4H_{11}^+ \qquad (24)$$

The appearance of $B_4H_{11}^+$ at the very low source pressure of B_2H_6 indicates that this reaction probably occurs for every collision of a $B_2H_5^+$ ion with a B_2H_6 molecule. Quenching of the reaction product by methane must also occur rapidly. The apparent stabilization energy of $B_4H_{11}^+$ obtained from temperature-dependence experiments is −1.3 kcal/mol. If equilibrium were achieved in the source in the short time available for reaction, this stabilization energy should be equivalent to the standard enthalpy change for reaction 24. From thermochemical considerations we have for reaction 24, $K_{eq} \geqslant I_{(B_4H_{11}^+)}/I_{(B_2H_5)^+}P_{(B_2H_6)} \geqslant 1.3 \times 10^6$ at 80°K. Using the decomposition of cyclobutane ($C_4H_8 \rightarrow 2C_2H_4$) as a model reaction, we estimate for reaction 24, $\Delta S° = -35 \pm 5$ eu. Combining this with $\Delta G° = -RT \ln K$ gives $\Delta H° \leqslant -4.1$ kcal/mol at 80°K. This calculation indicates that, unless the $\Delta S°$ for reaction 24 is unusual, the stabilization energy is only a fraction of the thermodynamic $\Delta H°$. In the thermochemical calculation an error in K_{eq} of five orders of magnitude will amount to an error less than 2 kcal/mol in $\Delta H°$. Thus we estimate for reaction 24 a value within the limits −4.1 ± 3.0 kcal/mol at 80°. Based on the preceding calculation, $B_4H_{11}^+$ should be thermally dissociated at temperatures at which CI sources are usually operated. Combining heats of formation of $B_2H_5^+$,[8] B_2H_6,[9] B_4H_{10},[10] and H^+[8] with $\Delta H°$ for reaction 24 gives for the proton addition reaction

$$H^+ + B_4H_{10} \longrightarrow B_4H_{11}^+ \quad \Delta H = -144 \pm 5 \text{ kcal/mol} \qquad (25)$$

or a proton affinity for B_4H_{10} of 144 ± 5 kcal/mol.

Discussion

In Table VI the proton affinities of B_2H_6 and B_4H_{10}, obtained in this study, are compared with similar data for B_5H_9, B_5H_{11}, and B_6H_{10} reported in the earlier paper.[1] It is evident that the more "saturated" boron hydrides are weaker bases than the "unsaturated" compounds. The proton affinity of B_2H_6 is close to that estimated through the assumption that the sum of the proton affinity and the ionization potential for a member of a series of structurally related molecules is constant.[1] The proton affinity of B_5H_{11} was not obtained in these experiments due to a limited temperature range available above the condensation point of the compound.

Table VI. Thermochemical Data for Protonated Boron Hydrides

Molecule	PA, eV	Ion	Heat of formation (kcal/mol)	Ref
B_2H_6	6.35 ± 0.20	$B_2H_7^+$	229 ± 5	This work
B_4H_{10}	6.25 ± 0.20	$B_4H_{11}^+$	238 ± 5	This work
B_5H_9	7.24 ± 0.26	$B_5H_{10}^+$	217 ± 6	1
B_5H_{11}	⩽7.5	$B_5H_{12}^+$		1
B_6H_{10}	8.46 ± 0.35	$B_6H_{11}^+$	194 ± 8	1

For the $B_5H_n^+$ species we observe the relative order in heats of formation $B_5H_{10}^+ < B_5H_8^+$ and $B_5H_{10}^+ < B_5H_6^+$. These comparisons are not in line with published data obtained by electron impact (EI) studies. The EI results for $B_5H_8^+$ (ΔH_f = 208 kcal/mol)[11] indicate this ion to be more stable than $B_5H_{10}^+$. However, the appearance potential of $^{11}B_5H_8^+$ from B_5H_9, as noted in the original work, remains in doubt since the determination may well refer to the species $^{11}B_4{}^{10}BH_9^+$, the parent ion with one ^{10}B atom. For the $B_4H_n^+$ species our results indicate that the heat of formation of $B_4H_9^+$ is less positive than that for $B_4H_7^+$ (Table V). This order is qualitatively in line with published data for these ions.[8] Stabilization of $B_4H_{11}^+$ in the proton transfer reaction of CH_5^+ with B_4H_{10} at low temperatures indicates that the zero point energy of $B_4H_{11}^+$ is below that for $B_4H_9^+ + H_2$. From this consideration the heat of formation of $B_4H_{11}^+$ is then ≤245 ± 5 kcal/mol.[12] The apparent stabilization energies of $B_4H_9^+$ observed in the CH_5^+–B_4H_{10} reaction show a pressure effect as indicated in Table V. Although some of the differences in ΔE may reflect experimental errors, it is reasonable to expect that at high source pressures increased quenching of the intermediate $(B_4H_{11}^+)^*$ will lead to $B_4H_9^+$ in a lower state of activation.

In some respects the chemistry of the $B_2H_n^+$ species may be compared to that of $C_2H_n^+$. In the hydrocarbon system consisting of 1% of C_2H_6 in CH_4, the following reaction has been confirmed at ambient temperatures[13]

$$CH_5^+ + C_2H_6 \longrightarrow C_2H_7^+ + CH_4 \qquad (26)$$

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(8) 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 26, U. S. Government Printing Office, Washington, D. C., 1969.

(9) "JANAF Thermochemical Tables," 2nd ed, NSRDS-NBS 37, U. S. Government Printing Office, Washington, D. C., 1971.

(10) D. D. Wagman, W. H. Evans, V. B. Parker, I. Harlow, S. M. Bailey, and R. H. Schuman, NBS Technical Note 270-3, U. S. Government Printing Office, Washington, D. C., 1968.

(11) J. J. Kaufman, W. S. Koski, and S. S. Wright, *J. Amer. Chem. Soc.*, **85**, 1369 (1963).

(12) T. P. Fehlner and W. S. Koski, *J. Amer. Chem. Soc.*, **85**, 1905 (1963).

(13) M. S. B. Munson and F. H. Field, *J. Amer. Chem. Soc.*, **87**, 3294 (1965).

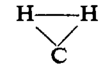
Furthermore, observation of $C_2H_7^+$ at these conditions implies that the decomposition[14]

$$C_2H_7^+ \longrightarrow C_2H_5^+ + H_2 \qquad (27)$$

has an activation energy which is probably greater than that for H_2 elimination from $B_2H_7^+$. Low-temperature ion-molecule reactions in C_2H_6 produce a species of m/e 59 which appears to be formed by the reaction $C_2H_5^+ + C_2H_6 \rightarrow C_4H_{11}^+$ (1972, unpublished work by this laboratory).

This is quite analogous to the reaction between $B_2H_5^+$ and B_2H_6. However, at normal source temperatures neither $C_4H_{11}^+$ nor $B_4H_{11}^+$ is observed within the limits of our sensitivity.

Proposed structures for $B_2H_7^+$ and $B_4H_{11}^+$ are illustrated in Figure 11. A number of other configurations are possible and theoretical calculations may help resolve these. The structure of $B_2H_7^+$ is suggested by analogy with CH_5^+, which is now believed to have C_s configuration consisting of three "normal" C–H bonds and one three center bond.



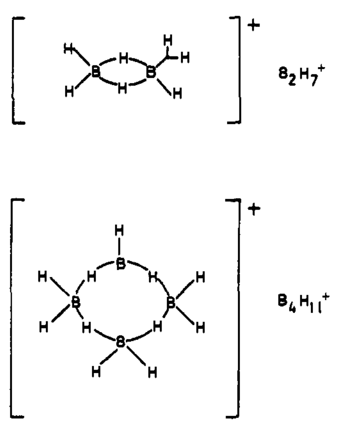


Figure 11. Possible structures for $B_2H_7^+$ and $B_4H_{11}^+$.

The structure for $B_4H_{11}^+$ is assumed to be a composite of $B_2H_5^+$ and B_2H_6 with four bridge hydrogen bonds and seven terminal B–H bonds. The small value of ΔH for formation of $B_4H_{11}^+$ from $B_2H_5^+$ and B_2H_6 suggests no significant net change in structural features of the reactants and product.

Acknowledgment. We are grateful for support by the Army Research Office—Durham, N. C., and the National Science Foundation (Grant GH 33637) through the Materials Science Center, Cornell University.

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(14) The ΔH has been estimated to lie between 0 and 9 kcal/mol. J. L. Franklin and F. H. Field, "Electron Impact Phenomenon and Properties of Gaseous Ions," Academic Press, New York, N. Y., 1957.

X-Ray Photoelectron Spectroscopic Studies on the Electronic Structures of Porphyrin and Phthalocyanine Compounds

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Abstract: We have measured the nitrogen 1s binding energies and some metal binding energies of porphyrin and phthalocyanine compounds by X-ray photoelectron spectroscopy. We find that this technique yields interesting new data. In particular, we find two kinds of nitrogen in tetraphenylporphine free base, differing in charge by about 0.2 e. We find the nitrogens of most metalloporphyrins to be similar to those of porphine base which lack protons. We find the two kinds of nitrogen in metal phthalocyanines to be identical with photoelectron spectroscopy. Finally, we find that the iron in the oxidized and reduced forms of iron porphyrin differ in charge by some 0.44 electron charges. On the whole, our results compare well with the theoretical predictions of Gouterman and coworkers.

It is already well known that X-ray photoelectron spectroscopy offers the possibility of measuring the charge distribution in molecular systems.[1-3] It thus provides a unique view of the electronic structure of a system, a view which is close to the basic theoretical ideas we use in discussing molecules. We have been applying the technique to various porphyrin and phthalocyanine compounds and we report some of our results herein.

It is unlikely that we shall be able to obtain a complete charge distribution for one of these molecules in the foreseeable future and, in this report, we shall restrict ourselves primarily to discussing the charges on the nitrogen atoms in the various compounds.

Porphyrin and phthalocyanine compounds have received a great deal of attention, partly because of their relevance to various biological systems, but most of the techniques heretofore available provide either information which is only indirectly related to the ground-state electronic structure, or information about only a portion of the electronic structure. X-Ray crystal-

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(1) K. Siegbahn, *et al.*, "ESCA–Atomic Molecular and Solid State Structure Studied by Means of Electron Spectroscopy," Almqvist and Wiksell, Uppsala, Sweden, 1967.

(2) J. M. Hollander and D. A. Shirley, *Annu. Rev. Nucl. Sci.*, **20**, 435 (1970).

(3) M. E. Schwartz, J. D. Switalski, and R. E. Stronski in "Electron Spectroscopy," D. A. Shirley, Ed., North-Holland Publishing Co., Amsterdam, 1972, p 605.