from a specific level and errors due to the "around the corner" effect may be introduced if the extinction coefficient for one vibrational level is much larger than that of its neighbors. The relatively large band pass used here was the best that our instrumentation could provide.

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Mass Spectrometric Investigation of the High-Temperature Reaction of Hydrogen with Boron Carbide[1]

by Sara J. Steck,[2] George A. Pressley, Jr., and Fred E. Stafford

Department of Chemistry and the Materials Research Center, Northwestern University, Evanston, Illinois 60201 *(Received June 24, 1968)*

The boron-containing gaseous molecules BH, BH_3, HBC_2, and $BH_2C_xH_{2x+1}$ ($x = 1$ and 2) have been identified as products of a high-temperature reaction of hydrogen with boron carbide; higher molecular weight boron–carbon–hydrogen molecules may have been present, but they could not be observed because of interference from hydrocarbons formed in the reaction. Evidence for BH_2 was not found. Concentrations of BH_3 and the two alkylboranes far exceeded the predicted equilibrium quantities. This phenomenon is thought to result from a steady-state reaction in the crucible, and a mechanism is suggested. The other molecules, BH and HBC_2, appeared to be present in near-equilibrium concentrations. Values for $D°(BH\text{-}H)$ and $D°(BH_2\text{-}H)$ are discussed; revisions are suggested. Secondary electron multiplier gains determined for H, H_2, and ^{11}B are in the ratio 1:3.5:19.2 for 6.5-kV ions. $D(H\text{-}BC_2)$ is determined to be 100 ± 10 kcal/mol.

Introduction

Tabulated thermodynamic data[3] suggest that the high-temperature reaction of hydrogen with boron carbide should yield such relatively simple molecules as BH, BH_2, and BH_3. All three of these species have been identified as transient intermediates, and various properties have been reported: for BH, both the uv[4] and vacuum uv[5] spectra have been subject to rotational analyses and the ionization potential was evaluated;[5] for BH_2, an electron impact ionization potential[6] has been obtained, and rotational analysis of the electronic spectrum has indicated a bent geometry in the ground state;[7] and for BH_3, the ionization potential[6–8] and the mass spectrum[9] have been measured. Because of the small number of electrons in these molecules, data for these species are particularly valuable for comparison with results of theoretical calculations.[10–14] Some discrepancies appear to exist between the limited experimental data and various theoretical treatments; for instance, the available thermodynamic data[3] for these hydrides do not agree with arguments used to explain the boron fluoride bond dissociation energies.[15]

Especially since the carboranes show greater thermal stability than do the boron hydrides, the high-temperature reaction of boron carbide with hydrogen might be expected also to yield boron–carbon–hydrogen species. In particular, the molecules BC_2 and B_2C

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observed by Verhaegen, *et al.*,[16] might react with hydrogen to form BC_2H and B_2CH which are isoelectronic with C_3 and BC_2, respectively. Higher hydrogen content species analogous to the $BX_2Si_nX_{2n+1}$ compounds ($X = F$, $n = 1, 2, 3$[17,18] and $X = Cl$, $n = 1$[19]), which have been synthesized using high-temperature molecules, would correspond to dissociated alkylborane dimers.

Identifications of boron–hydrogen and boron–hydrogen–carbon species formed in the high-temperature reaction of hydrogen with boron carbide, together with postulated mechanisms of formation and/or thermodynamic data and implications, are reported in this paper. An extensive high-temperature, high-molecular-weight carbon–hydrogen system extending to m/e 140 and beyond also was observed and will be reported elsewhere.[20]

Experimental Section

Spectra were obtained with a Nuclide Analysis Associates 12-in. radius, 60° sector Inghram-type high-temperature mass spectrometer.[21,22] Hydrogen (Matheson prepurified grade) was admitted to the spectrometer through a cylinder pressure regulator, a vacuum regulator (J. T. Baker Chemical Co.), a glass vacuum line with a ballast bulb and manometer, a Granville-Phillips (Boulder, Colo.) variable leak, and an Andonian Associates (Waltham, Mass.) leak. This line is then attached to the inlet into the spectrometer (Figure 1 in ref 9).

A tilting McLeod gauge, which was attached to the stainless steel tube leading into the instrument (Figure 1[9]), was used to measure the absolute hydrogen pressure. A boron nitride (Norton Co., Worcester, Mass.) tube served as an electrical insulator between the steel tube and the stem of the ATJ graphite (National Carbon Co.) reactor. Pressure of the hydrogen in the crucible was calculated using the McLeod gauge readings and conductance corrections[23] for the inlet system; four-mesh "high boron content" boron carbide from the Norton Co. was loosely packed over the bottom inlet into the reactor and three-quarters of the way up the crucible. Electron bombardment from two tungsten filaments heated the 15.9-mm i.d. reactor; the crucible assembly and heating filaments were surrounded by a set of tantalum shields to diminish heat radiation. A power-regulated high-voltage supply based on an Argonne National Laboratories design[24] greatly facilitated the experiments. Temperature was determined with a Leeds and Northrup disappearing-filament optical pyrometer which could be sighted on black-body radiation holes at the top and bottom of the graphite reactor; an emissivity correction of 0.84 was made for grayness of the hole and for attenuation by the intervening window. Products of the reaction effused through a 0.37-mm diameter orifice in the reactor cap.

To accommodate relatively high hydrogen pressures in the reactor, a 1-in. Edwards Speedivac mercury-diffusion booster pump was placed between the forepump and the three mercury-diffusion pumps of the differential pumping system.[9,22] This booster pump effectively lowers the backing pressure while it increases the forepump throughput.

A movable beam defining slit located between the crucible assembly and the ion source region was used to differentiate species arising from the crucible orifice from those which had collided with the instrument walls and the ion source assembly and from those which arose from the crucible lip or the tantalum radiation shields.

In the ion source region, a beam of ionizing electrons intersected the molecular beam arising from the crucible orifice. The ion source was normally operated with an ionizing electron voltage of 70 eV, with a total emission current of 1.2 mA, which corresponds to a trap current of about 10^{-5} A and with an ion-accelerating voltage of 4 kV. Appearance potentials were calibrated to the appearance potential of boron and were evaluated using the vanishing-current method.[25]

After mass analysis, ions were detected by both a 50% transmission grid collector and a secondary electron multiplier so that relative multiplier gains could be determined for intense peaks. The 16-stage multiplier used in the early experiments was normally operated with 3.9 kV across the dynode resistor string but the 20-stage multiplier used in later experiments was operated at 2.5 kV. Typical multiplier gains for the latter were: H^+, 1.25×10^4; H_2^+, 4.4×10^4; and B^+, 2.40×10^5. Other ions observed had gains of the order of 10^5.

Direct digital acquisition and computer treatment of data[26] were used in most experiments.

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Data

Ions observed in the mass spectra were identified on the basis of isotope ratios, shutter percentages,[27] and mass defect. Figure 2 in ref 22 shows the resolution of ion peaks at the same nominal mass in the monoborane ion group; Figure 1 shows the resolution of HCl^+, C_3^+, and HBC_2^+, all at *m/e* 36. Species containing one boron and three or more carbons cannot be so resolved. Spectra were generally measured at 70 eV because of the small ion intensities found for many of the species.

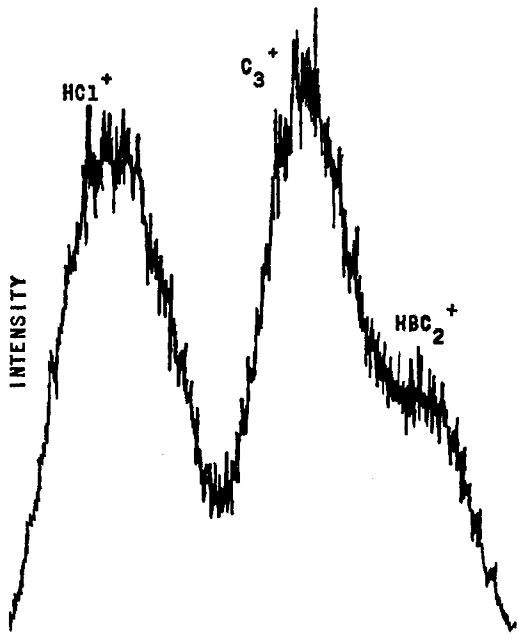

Figure 1. Mass peak 36; well-defined peaks are HCl^+ and C_3^+; the shoulder on the right-hand side is HBC_2^+.

Large percentage shutter effects[27] were observed for ions corresponding to the neutral species C_3, BC_2, B_2C, and B before hydrogen was admitted to the reactor; all of these species have been reported previously.[16,21] Ions from the species BC, which also has been reported,[16] were not clearly resolved in these experiments because of interference at *m/e* 22 and 23.

A mass spectrum of the boron-containing ions observed after hydrogen was introduced into the crucible is given in Table I. Although no positive mass defect (*i.e.*, boron-containing) ions could be resolved at ion peaks at *m/e* ~50, the shutter percentages[27] on the high-mass side (positive mass defect) of the hydrocarbon peaks were generally greater than that observed at the top of the hydrocarbon peak. This behavior suggests that higher molecular weight boron-containing species were present but not clearly observable with the resolution available.

Table I: Mass Spectrum of Boron-Containing Species Formed in the Reaction of 0.19 Torr of Hydrogen with High-Boron-Content Boron Carbide at 2427°K[a]

m/e	Species	Relative intensity
11	$^{11}B^+$	100
12	$^{11}BH^+$	4.6
13	$^{11}BH_2^+$	14.6
14	$^{11}BH_3^+$	4.6
22[b]	$^{10}BC^+$	0.04
24	$^{10}BCH_2^+$, $^{11}BCH^+$	0.29
25	$^{11}BCH_2^+$, etc.	0.52
26	$^{10}BCH_4^+$	1.6
27	$^{11}BCH_4^+$	6.0
28	$^{11}BCH_5^+$	0.26
29[c]	$^{11}BCH_6^+$?	0.06
33	$^{10}B_2C^+$	0.50
34	$^{11}B_2C^+$, $^{10}BC_2^+$, $^{10}B_2CH^+$	3.6
35	$^{11}BC_2^+$, $^{11}B_2CH^+$, $^{10}BC_2H^+$	11.6
36[d]	C_3	10.9
36[d]	$^{11}BC_2H^+$, etc.	6.8
37[e]	$^{11}BC_2H_2^+$	0.49
38	$^{10}BC_2H_4^+$	0.10
39	$^{11}BC_2H_4^+$	0.41
40	$^{11}BC_2H_5^+$	0.30
41[c]	$^{11}BC_2H_6^+$?	0.06

[a] Run 671211-33 taken at 70 eV and not corrected for secondary electron multiplier gain. [b] A large interfering photo-ion effect[21] is observed at *m/e* 23. [c] Shutter percentages[27] of these mass peaks are half those of the preceding peaks. [d] See Figure 1. [e] The ion intensity of this mass peak in this particular spectrum seems anomalously large if compared to other spectra.

Both hydrogen pressure and temperature dependence studies were made of the ions given in Table I. For law of mass action studies, ion intensities were measured at three hydrogen pressures (*ca.* 0.008, 0.06, and 0.19 Torr in the reactor) at each of six temperatures between 2100 and 2400°K. Ion intensities, except those of B^+ and C_3^+, normally showed a hydrogen pressure dependence of approximately $P(H_2)^{1/2}$; between the two higher pressures, BH_3^+, BH_2^+, and BH^+ ion intensities did show a hydrogen dependence between $P(H_2)^{2/2}$ and $P(H_2)^{3/2}$ at two of the temperatures investigated. Difficulties in measuring the small ion intensities, possible saturation of the secondary electron multiplier, and length of time required for measurements cannot account for such large deviations from the law of mass action as are indicated for ions (and therefore the neutral progenitors) that contain three to six hydrogen atoms. Because of temperature gradients as large as 100–200° between the radiation holes at the top and bottom of the reactor, temperature dependence of the ion intensities is not as well defined as desired. Changes of the ion intensities with temperature, however, roughly divided them into the following groups: *m/e* 41–37, *m/e* 36–33, *m/e* 28–22, and *m/e* 14–10.

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(27) "Shutter percentage" is the ratio of the molecular beam intensity to the total ion intensity at a given mass peak. Argon, for example would show about a 4% shutter effect at these temperatures. Ions from a reactive species, one that is rapidly pumped by collisions with the vacuum chamber walls, would have a 100% shutter effect.

Interpretation of Data

Identification of Neutral Progenitors. Formation of the ions listed in Table I by ion–molecule reactions in the source region or by collisions of molecules in the molecular beam is ruled out by the low source pressures (3×10^{-6} Torr), molecular flow conditions at all but the highest pressures studied, and the one-half power hydrogen pressure dependence of many species. Any ion–molecule or molecular beam reaction mechanism requires a first, second, or third power dependence, which was not observed.

Boron-containing ions that were clearly resolved from the hydrocarbon ions at the same nominal masses can be discussed in three separate groups. The first of these groups includes those peaks at *m/e* 41–33. Ions at *m/e* 33–35 were observed before hydrogen was introduced into the reactor and arose from B_2C and BC_2. Isotope distributions[28] (Table I) suggest that the ions at *m/e* 36–41 contain only one boron atom, *i.e.*, $BC_2H_x^+$. The logical neutral progenitor of these ions is an alkylborane such as $BH_2C_2H_5$ or $BH(CH_3)_2$. Two alkylboranes, *asym*-dimethyldiborane and ethyldiborane, are among the best model compounds from which to infer fragmentation patterns for the proposed progenitors; other model compounds are the BX_3 molecules (X = H, F, Cl, Br, and I) and $BF_2Si_2F_5$. Accordingly, relative ion intensities for selected peaks in the $BC_2H_x^+$ and BCH_x^+ ion groups of *asym*-dimethyldiborane[28] and ethyldiborane[28] are listed in Table II. The large relative intensity at *m/e* 41 in the *asym*-dimethyldiborane spectrum (line 1) suggests that the probable fragmentation pathway of $BH(CH_3)_2$ would be loss of hydrogen, a fragmentation pattern that would be expected for a BX_2Y molecule in which the B–CH_3 bond is stronger than the B–H bond.[29] The ethyldiborane ion peaks (line 2) suggest that the principal fragmentation pathway for $BH_2C_2H_5$ would be loss of a methyl group to give the most intense peaks in the BCH_x^+ ion group; this fragmentation pattern would be predicted for a molecule in which the B–C and B–H bonds are stronger than the C–C bonds. This type of spectrum is observed[17] for $BF_2Si_2F_5$, a molecule in which the Si–Si bond is the weakest. The observed spectrum (line 3) shows smaller ion intensity at *m/e* 41 than at *m/e* 40 and 39. This behavior is not that of a B–H bond being most easily cleaved (*asym*-dimethyldiborane) and corresponds more closely to that shown by ethyldiborane. Accordingly, ethylborane $BH_2C_2H_5$ is inferred to be the species present; the analogous molecule $BF_2Si_2F_5$ has been formed (at low temperatures) from high-temperature species by Timms, *et al.*[17]

Table II: Comparison of the Relative Intensities of Ion Peaks from *asym*-Dimethyldiborane and Ethyldiborane with Those Observed in the High-Temperature Reaction of Hydrogen with Boron Carbide

m/e	41	40	39	27	26
asym-Dimethyldiborane[a]	100	58	35	30	15
Ethyldiborane[a]	9	18	15	100	59
Observed spectrum	1	5	7	100	27

[a] See ref 28.

The most intense boron–carbon–hydrogen ion peak was resolved on the high-mass side of the C_3^+ ion peak as shown in Figure 1. This ion was resolved only above 2300°K and at the higher hydrogen pressures used. Assignment of this ion is logically HBC_2^+ from neutral HBC_2, a molecule that is isoelectronic with C_3. A half-power hydrogen pressure dependence supports this assignment.

Difficulty encountered in stripping the boron isotope ion contributions from *m/e* 33 through 36 gives some evidence for the molecule HB_2C, which is isoelectronic with BC_2, or possibly H_2B_2C, which is isoelectronic with C_3.

The second ion group in which ions with positive mass defects relative to the hydrocarbon background were resolved is *m/e* 29–22. None of these ions, with the possible exception of BC^+, was observed until after hydrogen was introduced into the reactor. Comparison of the ratio $I(27^+)/I(26^+)$ to the known isotopic distribution of boron[28] shows that the ions are members of the BCH_x^+ rather than the $B_2H_x^+$ series. Table II, line 2, shows that appreciable contributions to the intensities of these peaks would be expected from fragmentation of ethylborane, the proposed progenitor of the higher molecular weight boron–carbon–hydrogen ions. The relative intensities in the mass spectrum of ethyldiborane,[28] however, suggest that ethylborane probably does not account for all the BCH_x^+ ion intensity; this argument suggests that BH_2CH_3 also is present. Timms[19] has reported the synthesis of the analogous compound BCl_2CCl_3 by two different high-temperature reactions.

The presence of HBC, a molecule isoelectronic with C_2, need not be invoked to explain the ion intensity at *m/e* 24.

Mass peaks 14–10 represent the last group of boron-containing ions. Since all of these ions may be formed by a fragmentation process, rough appearance potentials (AP's) were obtained and used to help determine the progenitors. Resolution of these peaks from the adjacent ones due to hydrocarbon ions[22] permitted measurement of appearance potentials.

The observed appearance potential for BH_3^+ is 11.5 ± 0.5 eV (uncertainties quoted are average deviations). That this ion is formed from neutral

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BH_3 is suggested by the agreement with the two reported electron impact values of the ionization potential, 11.4 ± 0.2[6] and 12.32 ± 0.1[8] eV. This ion, moreover, is not usually seen in boron hydride or alkylborane mass spectra.[28] Temperature and hydrogen pressure dependence experiments also suggest that it is not formed from higher molecular weight boron-containing ions.

An AP of 12.3 ± 0.5 eV was found for BH_2^+; this is considerably greater than the reported ionization potential of 9.8 ± 0.2 eV[6] and more nearly approaches the value 12.95 ± 0.05 eV[8] for the AP of BH_2^+ from BH_3. The AP for the formation of BH_2^+ from either BH_2CH_3 or $BH_2C_2H_5$ should be about the same or higher; large contributions from these alkylboranes to the BH_2^+ ion intensity, however, are not expected by analogy with alkyldiborane spectra.[29] That no more than 5–10% of the observed BH_2 intensity could be due to neutral BH_2 is indicated by (1) the high appearance potential, (2) the agreement of the present experimental ratio for $I(BH_3^+)/I(BH_2^+)$ with that previously observed[9] for BH_3 formed from diborane, and (3) the constancy of the ratio $I(BH_3^+)/I(BH_2^+)$ with changes in temperature and hydrogen pressure. This limit does not preclude the presence of BH_2 if it undergoes extensive fragmentation upon ionization.

A break in the BH^+ ionization efficiency curve suggests that this ion is formed both by ionization of neutral BH and by decomposition of another ion such as BH_3^+. Spectroscopic measurements give an ionization potential of 9.77 eV[5] for BH; the present electron impact value is 9.8 ± 0.5 eV. A break in the ionization efficiency curve gives an appearance potential of 13.7 ± 1.0 eV for the second process; this is close to the value 13.66 ± 0.02 eV[8] observed for the formation of BH^+ from BH_3.

Molecules deduced to be present when hydrogen is treated with boron carbide at high temperatures are therefore, BH, BH_3, HBC_2, BC_2H_7, and probably BCH_5. Some evidence for $BC_3H_x^+$ ions was found, but these and higher molecular weight species could not be resolved from the hydrocarbons formed.[20] Contributions from the free-radical BH_2 to BH_2^+, if any, were masked by fragmentation.

Partial Pressures. Observed ion currents were reduced to partial pressures and compared with values calculated from tabulated[3] equilibrium constants. The relationship between observed ion intensity and partial pressure $P(X)$ is

$$P(X) = [I^+(X)T]/[\gamma(X_i)\sigma(X)S]. \qquad (1)$$

$I^+(X)$ is the sum of all ion intensities due to X. Lack of knowledge of the fragmentation pattern of the molecule can introduce error into the calculation; even for a small molecule such as BH_3, the total ion intensity with 70-eV ionizing electrons is about four times that of the parent ion.[9] T is the temperature of the reactor. $\gamma(X_i)$ is the secondary electron multiplier gain for a given ion. It was measured for a number of ions for which it is then known within 10%; for ions of low intensity or for ions at mass peaks where interference occurred, it was estimated by analogy and is probably correct to within 50%. $\sigma(X)$ is the cross section for ionization of X. Few experimental results are available for absolute cross sections and most of them are estimated in one of several ways.[30,31] Error in these numbers could be a factor of 2, especially for molecules where the cross section is assumed to be the sum of the atomic cross sections. The values of γ and σ used in the calculations are tabulated in Table III. S is the instrument sensitivity. Three means used to estimate it were comparison of: (1) the boron ion intensities to tabulated partial pressures of boron,[3] (2) the hydrogen atom to hydrogen molecule ion intensity ratios to equilibrium constants[3] for the re-

Table III: Multiplier Gains and Ionization Cross Sections Used to Calculate Partial Pressures

Species	Multiplier gain, γ	Cross section, σ
H	1.25×10^4	0.76[a]
H_2	4.4×10^4	1.1[b]
B	2.40×10^5	3.2[a]
BH	2.4×10^5	3.96[c]
BH_2	2.4×10^5	4.72[c]
BH_3	2.4×10^5	5.58[c]
HBC_2	1.8×10^5	9.8[c]
BH_2CH_3	1.8×10^5	9.9[c]

[a] See ref. 30 and 31. [b] Experimental valueas cited in ref 31. [c] Cross section is found by summing the cross sections of the atoms in the molecule; difficult to determine multiplier gains for species such as HBC_2 are assumed to be the same as for a related species such as BC_2.

Table IV: Instrument Sensitivities Calculated from Boron Ion Intensity, Hydrogen Atom/Hydrogen Molecule Intensity Ratio, and Hydrogen Pressure Measurement[a]

Hydrogen pressure	I	II	III
B[b] sensitivity	9.7×10^{-8}	1.1×10^{-7}	7.6×10^{-8}
$\frac{H^c}{H_2}$ sensitivity	8.5×10^{-8}	1.6×10^{-7}	1.9×10^{-7}
H_2[d] sensitivity	1.4×10^{-6}	1.1×10^{-6}	8.5×10^{-7}

[a] Run 671209. See Table V for the hydrogen pressures, T = 2280°K. [b] Calculated using eq 1 with the partial pressure from JANAF[3] and the observed boron ion intensity. [c] Calculated using eq 1 for the ratio of the intensities of H to H_2 and the appropriate equilibrium constant. [d] Calculated using eq 1 and the pressure of hydrogen read from the McLeod gauge, corrected for conductance effects and dissociation of the hydrogen.

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Table V: Comparison of Observed and Calculated[a] Partial Pressures (atm) for Some Species Formed in the High-Temperature Reaction of Hydrogen with Boron Carbide at 2280°K[b]

	I		II		III	
	Obsd	Calcd	Obsd	Calcd	Obsd	Calcd
H_2	7.6×10^{-5}		2.3×10^{-4}		4.8×10^{-4}	
BH[c]	2.6×10^{-8}	7.2×10^{-8}	5.8×10^{-8}	1.2×10^{-7}	4.6×10^{-8}	1.8×10^{-7}
BH_2[d]	$<1.3 \times 10^{-8}$	1.5×10^{-7}	$<3.5 \times 10^{-8}$	4.4×10^{-7}	$<1.6 \times 10^{-8}$	9.2×10^{-7}
BH_3[e]	1.4×10^{-7}	4.6×10^{-11}	3.2×10^{-7}	2.3×10^{-10}	1.8×10^{-7}	7.3×10^{-10}
HBC_2[f]	5.0×10^{-8}		7.7×10^{-8}		5.9×10^{-8}	
BH_2CH_3[g]			7×10^{-8}	1×10^{-13}		

[a] Calculated using equilibrium constants from ref 3; See text. [b] Run 671209. [c] Observed intensity of ion is assumed to be one-half that at $^{11}BH^+$ multiplied by 1.25. [d] Observed intensity is assumed to be less than one-tenth that at $^{11}BH_2^+$ multiplied by 1.25. [e] Observed intensity of ion is assumed to be five times that observed at $^{11}BH_3^+$. [f] Observed intensity is assumed to be intensity at $^{11}BC_2H^+$ multiplied by 1.25. [g] From run 671211 with an average temperature of 2342°K and with a hydrogen pressure approximately equal to pressure II. Observed intensity is assumed to be one-half intensity at m/e 27$^+$ ($^{11}BH_2CH_2^+$). Calculated pressure is estimated as discussed in text at eq 2.

action $H_2(g) \rightarrow 2H(g)$, and (3) the hydrogen molecule ion intensities to the hydrogen pressures read from the McLeod gauge and corrected for the inlet tube conductance[23] and the dissociation of the hydrogen molecule. Three sets of sensitivities so calculated for one temperature are tabulated in Table IV. The first two methods give sensitivities that agree within a factor of 2, but the third method differs from the other two by about a factor of 10. The sensitivities calculated by each method were essentially constant with changes in temperature but varied with changes in hydrogen pressure (Table IV).

Several problems were responsible for the difficulties encountered in calculating the instrument sensitivity. The boron sensitivity varied because at constant temperature, the boron ion intensity fluctuated by as much as 50% with hydrogen pressure; the intensity change may have resulted from depletion of boron on the surface of the sample. The H/H_2 ratio sensitivity suffered from difficulty in measuring the H_2 molecular beam ion intensity which was only 3% of the total. This sensitivity also seemed to reflect some saturation of the secondary electron multiplier. The hydrogen pressure sensitivity contains error from the uncertainty in the McLeod gauge pressure readings and from the ill-defined conductance effect corrections for the loosely packed reactor.

The H/H_2 ratio sensitivity was used to calculate the observed pressures in Table V. For the particular data used to construct Tables IV and V, the intensities of the boron ion and the boron-containing ions were smaller at the highest hydrogen pressure than at the intermediate pressure. Consequently, use of the H/H_2 ratio sensitivities suggests lower partial pressures for all of these species at the highest hydrogen pressure whereas, use of the boron sensitivities gives highest pressures for all species at the highest hydrogen pressure.

On the basis of these considerations, especially that of uncertainty in S, the most probable error in the absolute pressures is estimated to be a factor of 20. The "literature" pressures given in Table V are calculated from tabulated[3] equilibrium constants but depend on hydrogen pressures calculated using S. Some of the error in S, therefore, cancels in the ratio of observed to literature pressures; expected uncertainty in this ratio is a factor of 5–6.

Comparison of the calculated and observed pressures in Table V suggests that the BH molecule is, within a factor of 3, present in the predicted[3] equilibrium concentrations. The upper limit for the partial pressures of BH_2 is low by a factor of 10; this difference by itself, particularly if BH_2 fragments extensively, does not exclude the possibility that neutral BH_2 is present in the reactor. Observed partial pressures for BH_3, surprisingly, are several orders of magnitude larger than the calculated equilibrium amounts. A comparison for HBC_2 is not available.

To estimate the thermodynamic concentration of the alkylboranes BH_2R ($R = CH_3, C_2H_5$) at these temperatures and pressures, the following calculations were made. $D(BH_2–H)$ and $D(BH_2–R)$ were assumed to be equal, which makes $\Delta H°$ for the reaction

$$BH_3 + R \rightarrow BH_2R + H \qquad (2)$$

equal to zero. Also, the differences in the free-energy functions, Δfef, where

$$fef = \frac{G°_T - H°_{298}}{T}$$

are estimated to be 7 eu by analogy to that[3,32] for the reaction

$$CH_4 + CH_3 \rightarrow C_2H_6 + H \qquad (3)$$

The difference is assumed to be independent of temperature. Use of this estimate in the relation

$$\Delta H°_{298} = -RT \ln K - T\Delta fef \qquad (4)$$

together with concentrations of BH_3, CH_3, and H

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(32) G. N. Lewis and M. Randall, "Thermodynamics," revised by K. S. Pitzer and L. Brewer, McGraw-Hill Book Co., Inc., New York, N. Y., 1961, p 682.

Table VI: Observed Reaction Enthalpies, Heats of Formation, and Atomization Energies (kcal/mol)[a]

Molecule	Chemical equilibrium	$\Delta H°_{298}$	$\Delta H_f°_{298}$	$\Delta H_{at}°_{298}$
B	$0.25B_4C(s) \rightleftarrows B(g) + 0.25C(s)$	133 ± 5	130	
BH	$B(s, B_4C) + H(g) \rightleftarrows BH(g)$	56 ± 5	108	77
	$B(g) + H_2(g) \rightleftarrows BH(g) + H(g)$	26 ± 5	107	
HBC_2	$BC_2(g) + H_2(g) \rightleftarrows HBC_2(g) + H(g)$	4 ± 5	130	397

[a] Third-law calculations for 23 separate points representing 11 different temperatures were made to obtain each $\Delta H°_{298}$ recorded. The uncertainties are accuracies; standard deviations were ±1 to ±3 kcal/mol. All data used in the cycle to calculate $\Delta H_f°_{298}$ and $\Delta H_{at}°_{298}$ come from ref 3.

calculated from the observed hydrogen pressure and tabulated[3] equilibrium constants, gives a calculated $P(BH_2CH_3)$ equal to 1×10^{-13} atm, the observed pressure (Table V) is 7×10^{-8} atm. The C_2H_5 partial pressure should be much lower than that of CH_3; consequently, the difference between the calculated and observed partial pressures is expected to be even larger than for BH_2CH_3. This discrepancy is greater than any reasonable experimental error. To account for it, $D(BH_2–CH_3)$ or $D(BH_2–C_2H_5)$ must be 50–60 kcal/mol larger than $D(BH_2–H)$ and/or the Δfef must be in error by 25 eu; this is unlikely.

Table V gives only a small fraction of the data points measured; however, the formalism of third-law calculations[21] with eq 4 can be utilized to summarize all of the measurements. Apparent equilibrium constants were calculated using eq 1. Free-energy functions for $B_4C(s)$, $C(s)$, $B(g)$, $BH(g)$, $BH_2(g)$, $BH_3(g)$, $H_2(g)$, and $H(g)$ were taken from the JANAF compilation;[3] the difference in fef between $BC_2(g)$ and $HBC_2(g)$ was estimated to be equal to that between $C_2(g)$ and $C_2H(g)$.[3] In this formalism, a factor of 10 in a partial pressure or in the equilibrium constant at these temperatures results in a 10-kcal/mol difference in the calculated $\Delta H°$, *i.e.*, $RT \ln 10 \approx 10$ kcal/mol.

The heat of sublimation for boron estimated by this method (130 ± 5 kcal/mol, Table VI) is within experimental error of that presently accepted by JANAF[3] (132.8 ± 4 kcal/mol); values at the lowest hydrogen pressures were about 4 kcal/mol more exothermic than those for the highest pressures; a trend with changing temperature was not observed. The calculated heat of formation for BH (107 ± 5 kcal/mol) is only slightly more endothermic than that (105.8 ± 2.0 kcal/mol) derived from the spectroscopic value of $D(B–H) = 3.39$ eV;[3,12] no systematic trends with changing temperature or hydrogen pressure were noted for either of the two reactions used in calculating the values given in Table VI. Agreement of results for the above two species with other experimental work suggests that the thermodynamic properties given in Table VI for the new molecule HBC_2 are accurate within ±10 kcal/mol since HBC_2, as well as BH, is observed to obey the law of mass action.

For BH_3, enthalpies of reaction were calculated for the four isomolecular reactions

$$B(s) + 2H_2(g) \rightarrow BH_3(g) + H(g)$$

$$2B(s) + 2H_2(g) \rightarrow BH_3(g) + BH(g)$$

$$B(g) + 3H_2(g) \rightarrow BH_3(g) + 3H(g)$$

$$BH(g) + 2H_2(g) \rightarrow BH_3(g) + 2H(g)$$

As expected from the failure of $I(BH_3^+)$ to vary with hydrogen pressure according to the law of mass action, values of the heat of formation of BH_3 calculated from the heats of reaction for the above four equations and from tabulated[3] data varied systematically with pressure; trends in the values were observed also for temperature and the reaction calculated. In all cases, the $\Delta H_f°$ so calculated were 20–40 kcal/mol more exothermic than the accepted value[3] of 25.5 ± 10 kcal/mol. This means that averaged over all sets of measurements made, BH_3 is present in quantities 10^2–10^4 greater than that expected for equilibrium conditions; this difference is at least a factor of 10 beyond experimental error.

Measurements[33] similar to these on $CH_2(g)$ led to a heat of formation that is 13.5 kcal/mol more exothermic than that deduced from recent, reliable photoionization work;[34] in this case also, the CH_2 thus appears to be present in 10- to 30-fold excess over the equilibrium quantity.

Formation of the Gaseous Molecules. That the observed partial pressures for borane and the alkylboranes are so much larger than those calculated from established thermodynamic data is unexpected in two ways. First, because of the way the boron carbide is packed in the reactor, molecules are expected to undergo 10^4 wall collisions. Second, these complicated molecules that are present in greater than equilibrium quantities have been formed from the elements.

The most reasonable explanation of the present results seems to be the steady-state formation of radicals and other reactive intermediates in larger than equilibrium quantities; this effect is perhaps aided by

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(33) W. A. Chupka, J. Berkowitz, D. J. Meschi, and H. A. Tasman in "Advances in Mass Spectrometry," Vol. II, R. M. Elliott, Ed., The Macmillan Co., New York, N. Y. 1963, pp 99–109.

(34) W. A. Chupka and C. Lifshitz, *J. Chem. Phys.*, **48**, 1109 (1968).

the temperature and pressure gradients in the cell, or those between the cell and the hydrogen inlet tube. Analogous work with the carbon–hydrogen systems[20,33] indicates such a kinetically controlled reaction. The one-half power hydrogen pressure dependences of $P(BH_3)$ and $P(BH_2CH_3)$ suggest that BH, which seems to be in equilibrium with the hydrogen, is involved in the formation mechanism of these molecules. Observed reactions[35,36] of the isoelectronic species C suggest the following insertion reactions[37] $BH + H_2 \rightarrow BH_3$ and $BH + CH_4 \rightarrow BH_2CH_3$ as steps in the mechanism. Both reactions are expected to be exothermic by 80–100 kcal/mol and, therefore, are energetically favorable. The reaction $BH + H_2 \rightarrow BH_2 + H$ almost certainly is endothermic (see below) and is not expected to occur; this is in agreement with the fact that BH_2 is not observed.

That these molecules, once formed, do not come into equilibrium with the condensed phase rapidly is, in retrospect, not surprising. This phenomenon has been observed also for $BC_2(g)$ in contact with solid boron carbide–graphite mixtures.[16] A kinetic barrier to the decomposition of hydrocarbons on hot graphite surfaces also is known.[20,33,38,39]

Discussion

Although no directly comparable work on the high-temperature boron–carbon–hydrogen and boron–hydrogen systems has been done, related studies exist. Work by Verhaegen, *et al.*,[16] showed small amounts of BC, B_2C, and BC_2 in the gas phase above boron carbide at ~2000°K; hydrogen-containing derivatives of these molecules that are likely to be formed are those isoelectronic with C_2, BC_2, and C_3. Of these proposed molecules, definite experimental evidence was found only for HBC_2. Thermodynamic estimates made for this molecule suggest a heat of atomization of 397 ± 10 kcal/mol. Adding $D°_0(C_2) = 143$ kcal/mol,[3] $D°_0(BC) = 106$ kcal/mol,[3] and $D°_0(BH) = 78$ kcal/mol[3] and dividing the sum into the atomization energy for HBC_2 leads to a calculated resonance stabilization of 1.2; this value can be compared to 1.12 estimated for C_3 and 1.18 estimated for BC_2.[16] (The stabilization of HBC_2 would be the same even if the hydrogen is assumed to be bonded to carbon instead of boron because $D°_0(CH) = 81$ kcal/mol.[3] Even if the atomization energy were only 377 kcal/mol [*i.e.*, $D(H–BC_2) = 80$ kcal/mol instead of 100 kcal/mol], the calculated resonance stabilization would be 1.15.

Other resolved boron–carbon–hydrogen ions have been assigned to alkylborane progenitors. Although ethyl- and methylboranes are known as dimers at low temperature, reasonable thermodynamic estimates indicate that they should not be observable under the present conditions. An analogous molecule BCl_2SiCl_3 also has been formed in high-temperature flow system reactions;[19] molecules corresponding to the formulas $BF_2Si_xF_{2x+1}$ (x = 1, 2, and 3)[17,18] have been synthesized at low temperatures by cocondensation of the high-temperature species BF and SiF_2 with SiF_4 and BF_3.

Table VII: Bond Dissociation Energies (kcal/mol) of Borane

Bond	JANAF[a]	Wilson and McGee[b]	Jordan and Longuet-Higgins[c]
B–H	78	84	76
BH–H	110	90	66
BH_2–H	75	83	102
$\Sigma = A$(B–3H)	263	257	244

[a] Reference 3. [b] Reference 8. [c] Reference 10.

Experimental evidence for BH and BH_3, but not for BH_2, is contrary to predictions made with the successive bond dissociation energies calculated from electron impact data for borane.[3,8] Thermodynamic results selected by JANAF[3] (column 1 of Table VII) include electron impact values for D(BH–H) and D(BH_2–H); D(B–H) is spectroscopically determined; and A(B–3H), the atomization energy of borane, is established by the heat of vaporization of boron (132.8 ± 4 kcal/mol), the dissociation energy of hydrogen (104.200 ± 0.001 kcal/mol), and the heat of formation and the dissociation energy of diborane (9.8 ± 4.0, 40 ± 10 kcal/mol). Thus, if D(B–H) is accepted as correct, the sum [D(BH–H) + D(BH_2–H)] must be equal to 185 kcal/mol. Electron impact data of Wilson and McGee[8] (column 2 in Table VII) are constrained to fit a slightly different atomization energy for BH_3; this second study gives a result for D(BH–H) different by about 1 eV. This divergence of electron impact data, the lack of evidence for BH_2 in this experiment, and theoretical treatments suggest that further revision of the accepted bond dissociation energies is necessary. Jordan and Longuet-Higgins,[10] using an extrapolation of N–H and C–H parameters, obtained the values given in column 3 in Table V; their treatment does not depend on the recently corrected D(CH–H) and D(CH_2–H)[34,40] and, in fact, correctly predicts the newly determined values. Their calculations for the B–H bond energies, in contrast to the above values, suggest that D(BH_2–H) is the largest of the three, but they also predict a linear structure for BH_2, which is in disagreement with experi-

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(35) C. MacKay, J. Nicholas, and R. Wolfgang, *J. Amer. Chem. Soc.*, **89**, 5758 (1967).

(36) C. MacKay and R. Wolfgang, *ibid.*, **83**, 2399 (1961).

(37) For instance, J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1962.

(38) T. B. Reed in "Advances in High Temperature Chemistry," Vol. I, L. Eyring, Ed., Academic Press, New York, N. Y., 1967, pp 260–316.

(39) For instance, H. B. Palmer, J. Lahaye, and K. C. Hou, *J. Phys. Chem.*, **72**, 348 (1968).

(40) W. A. Chupka, *J. Chem. Phys.*, **48**, 2337 (1968).

ment.[7] Price, Passmore, and Roessler,[11] using isoelectronic comparisons, interpolated bond energies for all the first-row hydrides and their singly charged ions; this work gave values sensibly identical with those of JANAF[3] (Table VII, column 1). This treatment, however, is drastically affected by a number of more recently determined bond energies. In particular, the newly revised values for D(CH–H) and D(CH$_2$–H) of 101 and 108 kcal/mol[34,40] also change the corresponding bond dissociation energies of CH_2^+ and CH_3^+, the ions that are isoelectronic with BH$_2$ and BH$_3$. These and other new dissociation energies no longer lead to graphs with nearly parallel lines as drawn by Price, *et al.* The new curves, however, suggest that D(BH$_2$–H) is approximately equal to or greater than D(BH–H). The new interpolation is, therefore, in qualitative agreement with the Jordan and Longuet-Higgins treatment which suggests that D(BH$_2$–H) is larger than D(BH–H). An sp^2 hybridization argument used to explain the successive bond dissociation energies of BF$_3$ (D(BF$_2$–F) = 161 and D(BF–F) = 122 kcal/mol)[15] also suggests this ordering. To form BX$_2$, an s electron of BX must be promoted to a p orbital forming an sp^2 hybrid, but to form BX$_3$, no promotional energy is needed; this difference results in a larger BX$_2$–X bond energy. For BH$_2$, sp^2 hybridization is indicated by the bent ground state.[7] In view of these arguments and since the sum $[D(\mathrm{BH_2{-}H}) + D(\mathrm{BH{-}H})] = [A(\mathrm{B{-}3H}) - D(\mathrm{B{-}H})]$ is reasonably well known (Table VII, column I[3]), approximate values for the two bond dissociation energies can be deduced.[41]

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(41) NOTE ADDED IN PROOF. New results [E. S. Domalski and G. T. Armstrong, *J. Res. Nat. Bur. Stand.*, **72**, 133 (1968)] for ΔH_f (B$_{4.222}$C) do not affect the present calculations significantly.

The Electronic Density Distributions in Carbon Monoxide, Carbonyl Sulfide, and Carbon Dioxide

by Mark J. Hazelrigg, Jr., and Peter Politzer

Department of Chemistry, Louisiana State University in New Orleans,
New Orleans, Louisiana 70122 *(Received July 8, 1968)*

Plots of electronic density distributions are presented for CO, SCO, and CO$_2$. These are found to vary gradually in the order CO, SCO, CO$_2$, as expected. The validity of the transferability of bond properties concept is examined for the C–O bond in SCO and CO$_2$, and it is found to be only roughly valid in this case.

The carbon–oxygen bond represents one of the most important and widely found chemical linkages, one which occurs prominently in all branches of chemistry. It would be useful, therefore, to have a better understanding of the electronic structure of this bond and of the manner in which this structure (and hence the properties of the bond) is affected by the presence of various substituents on the carbon atom.

At least a start toward the achievement of this kind of understanding is now possible, through the availability of good wave functions for molecules containing the carbon–oxygen bond. The present work has involved the study of three such molecules: carbon monoxide, which has a pure C–O bond unaffected by the presence of any other atom; carbon dioxide, in which the effect of a second oxygen atom can be seen; and carbonyl sulfide, in which this second oxygen has been replaced by a sulfur atom, so that the relative effects of oxygen and sulfur atom substituents upon the C–O bond can be examined.[1]

The molecular wave functions used in this work were the self-consistent-field functions of McLean and Yoshimine.[2] They are believed to be close to the Hartree–Fock limit, which means that they should give

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(1) Extended-basis-set self-consistent-field wave functions, believed to be good approximations to Hartree–Fock functions, have been calculated for carbon monoxide by R. K. Nesbet, *J. Chem. Phys.*, **40**, 3619 (1964), and W. M. Huo, *ibid.*, **43**, 624 (1965). In both cases, the functions were analyzed in considerable detail, in terms of the expectation values of various molecular properties. An interpretative study of the electrostatic forces within the molecule has also been carried out by P. Politzer, *J. Phys. Chem.*, **69**, 2132 (1965).

(2) A. D. McLean and M. Yoshimine, "Tables of Linear Molecule Wave Functions," International Business Machines Corp., San Jose, Calif., 1967.