the increase in σ energy due to interaction of the π electrons is $11.3 + 13.6 = 24.9$ kcal/mol. It can be concluded that the important terms in the reorganization process are the π-bond energy and the $\sigma-\pi$ interaction energy.

The orbital energies and electronic distribution of the localized state of HBF_2 are presented in Tables III and IV. The occupied molecular orbitals of the localized model of the molecule are less stable than the corresponding values of the delocalized molecule. This destabilization as expected is more pronounced with the π-type orbitals (a_2 and b_1). Conversely the first vacant orbital becomes stabilized and is now composed solely of the boron p_z orbital. The population analysis reveals that the localization of the π electrons produces an expected net flow of electrons to the fluorines although there is a small σ-electron flow to the boron.

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Molecular Beam Mass Spectra and Pyrolysis of Pentaborane(9), Tetraborane Carbonyl, and Pentaborane(11). Formation and Mass Spectrum of Tetraborane(8)[1-3]
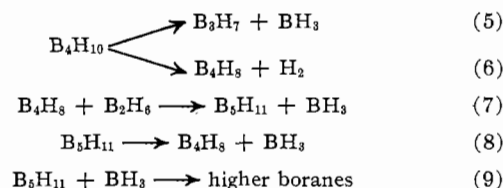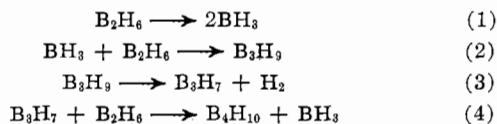
BY ROBERT E. HOLLINS AND FRED E. STAFFORD

A mass spectrometer with an integral flow reactor was used to study the pyrolysis of $^nB_5H_9$, $^{10}B_4H_8CO$, and $^{10}B_5H_{11}$ at very low pressures and to measure their molecular beam mass spectra. (a) The room-temperature molecular beam mass spectrum of B_5H_9 agreed with the spectrum obtained with an instrument with a conventional ion source. A preliminary study of its pyrolysis revealed no evidence for the formation of any reactive intermediates or other volatile boron containing products. (b) The molecular beam mass spectrum of B_4H_8CO differs drastically from that produced by a "conventional" ion source instrument due to pyrolysis in the conventional inlet and ion source systems. The B_4H_8CO ion decomposition (fragmentation pattern) parallels the known chemistry of tetraborane carbonyl. In the pyrolysis, B_4H_8 is the initial decomposition product; no monoborane or triborane species could be observed. Small amounts of pentaboranes and possibly diborane were observed but no higher boranes. Appearance potentials were measured for all the major ions due to B_4H_8CO. The mass spectrum of tetraborane(8) is reported and confirms its classification as a "stable" borane. (c) The molecular beam mass spectrum of B_5H_{11} differed slightly from the conventional, but there were indications of contributions to the latter by pyrolysis products formed in the ion source. A study of the pyrolysis of B_5H_{11} has shown B_4H_8 and BH_3 to be decomposition products. No triborane species could be observed; diborane and pentaborane(9) were observed, but no higher boranes could be detected under these experimental conditions.

Introduction

There has been considerable discussion of the postulated existence of BH_3, B_3H_7 and/or B_3H_9, and B_4H_8 intermediates in the pyrolysis of diborane and in the decomposition of tetraborane(10).[4-7]

A commonly accepted mechanism is

$$B_2H_6 \longrightarrow 2BH_3 \tag{1}$$
$$BH_3 + B_2H_6 \longrightarrow B_3H_9 \tag{2}$$
$$B_3H_9 \longrightarrow B_3H_7 + H_2 \tag{3}$$
$$B_3H_7 + B_2H_6 \longrightarrow B_4H_{10} + BH_3 \tag{4}$$

$$B_4H_{10} \begin{cases} \longrightarrow B_3H_7 + BH_3 & (5) \\ \longrightarrow B_4H_8 + H_2 & (6) \end{cases}$$
$$B_4H_8 + B_2H_6 \longrightarrow B_5H_{11} + BH_3 \tag{7}$$
$$B_5H_{11} \longrightarrow B_4H_8 + BH_3 \tag{8}$$
$$B_5H_{11} + BH_3 \longrightarrow \text{higher boranes} \tag{9}$$

Pearson and Edwards[8] studied the kinetics of the thermal decomposition of tetraborane(10) alone and in the presence of diborane and hydrogen. They proposed that tetraborane(10) could decompose by two simultaneous first-order mechanisms as shown in eq 5 and 6, since each reaction was first order in tetraborane(10). Pentaborane(11) could be formed by reaction 7 and diborane formed by the reverse of reactions 2 and 3. However, Dupont and Schaeffer[9] discovered that the conversion of tetraborane(10) to pentaborane(11) proceeded more rapidly in the presence of diborane. They suggested tetraborane(10) would form pentaborane(11) *via* reactions 6 and 7, since any triborane(7)

(1) Supported by the U. S. Advanced Research Projects Agency through the Northwestern University Materials Research Center.

(2) The acquisition and maintenance of the mass spectrometer facility was made possible by grants from the Materials Research Center, the AEC (Document No. COO-1147-32), and Northwestern University.

(3) Presented in part at the 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 1966 (see Abstract V-4), and at the 3rd Great Lakes Regional Meeting of the American Chemical Society, Northern Illinois University, DeKalb, Ill., June 5, 1969.

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formed from reaction 5 would be rapidly converted into tetraborane(10) by reaction 4.

Chemical evidence for the mono-, tri-, and tetraborane intermediates includes the existence of several Lewis base adducts, mainly with carbon monoxide.[4-7] Diborane reacts with many Lewis bases to form quantitative yields of the BH_3 adduct. Burg and Spielman[10] passed carbon monoxide through pentaborane(11) producing tetraborane carbonyl and borane carbonyl. Later, Schaeffer[11] prepared tetraborane carbonyl by treating carbon monoxide with tetraborane(10).

Brennan and Schaeffer[12,13] studied the reaction of tetraborane(10) with carbon monoxide and found the rate constants for the reactions $B_4H_{10} + CO$ and $B_4H_{10} + B_2H_6$ to be very similar and close to those obtained from the pyrolysis of B_4H_{10}. Both reactions were first order in tetraborane(10) and zero order in carbon monoxide or diborane. These data are consistent with the rate-controlling formation of the same intermediate in the two reactions, namely, tetraborane(8).

Recently, there has been direct physical evidence for the BH_3 intermediate from mass spectrometric studies of diborane[14-16] and borane carbonyl[17-21] and for B_4H_8 from tetraborane(10).[22]

Although tetraborane(8) was identified as a pyrolysis product from tetraborane(10), diborane, pentaboranes, and higher boranes also were formed; this prevented accurate measurement of the tetraborane(8) mass spectrum[22] and also prevented elimination of formation of B_3H_7 as a possible mechanism step. For this reason and because of the complexity of the mass spectrometric technique, it is desirable to examine the two other likely sources of tetraborane(8), B_4H_8CO and B_5H_{11}, in order that its mass spectrum and ultimately other properties can be measured and perhaps a high-yield synthesis can be found.

Since pentaborane(11) and especially tetraborane carbonyl are easily decomposed by hot surfaces, it was expected that their mass spectra[13,23] obtained with conventional[24] mass spectrometers would in fact be those of mixtures of the starting material plus reactive intermediates and decomposition products as was observed for tetraborane(10).[22,25] Molecular beam mass spectrometry eliminates this effect and is an indispensable part of a pyrolysis study in order that the spectrum of the original compound and any known, stable products be subtracted out from that of the pyrolysis product mixture.

Accordingly, this paper reports the results of molecular beam mass spectrometric studies of pentaborane-(9), tetraborane carbonyl, and pentaborane(11). The low-pressure pyrolyses of these compounds were studied in order to determine the initial intermediates, with particular hopes of obtaining a high-yield synthesis and mass spectrum of tetraborane(8).

Experimental Section

Synthesis and Purification of Starting Materials.—The initial samples of $^{10}B_4H_8CO$ and $^nB_5H_9$ were supplied by Professor Riley Schaeffer of Indiana University and by Dr. Arlan D. Norman, now at the University of Colorado. Upon the depletion of the $^{10}B_4H_8CO$ samples, $^{10}B_4H_8CO$ and $^{10}B_5H_{11}$ were synthesized using operations and manipulations involving standard high-vacuum techniques described elsewhere.[4,26-28]

$^{10}B_4H_8CO$ (96% ^{10}B and 4% ^{11}B)[29] was prepared by treating $^{10}B_5H_{11}$ with 15-20 atm of CO.[10,30,31] $^{11}B_5H_{11}$ was obtained from the controlled pyrolysis of $^{10}B_2H_6$ under previously described conditions.[32,33] $^{10}B_2H_6$ was prepared by the $LiAlH_4$ reduction of $^{10}BF_3 \cdot O(C_2H_5)_2$.[34,35] Calcium fluoroborate was converted to $^{10}BF_3 \cdot O(C_2H_5)_2$ following the procedure of Zedler.[36]

The B_4H_8CO and B_5H_{11} were purified[28] by fractional distillation in a specially designed[37] column. The B_4H_8CO and B_5H_{11} were collected separately from the column at -90 and $-80°$, respectively. The infrared spectrum[6] of a B_5H_{11} sample revealed no B_4H_{10} or B_5H_9 impurities ($<1\%$), and the subsequent mass spectrometric studies showed no hexaborane or higher boron hydrides present ($<0.05\%$) in the B_5H_{11} and B_4H_8CO samples. The samples were stored in liquid nitrogen ($-196°$) until time of use.

Mass Spectrometer.—An Inghram-type mass spectrometer[38,39] (built by Nuclide Corp., State College, Pa.), as modified, is identical with that used previously in studying borane intermediates.[15,40] In order to obtain a suitable flow rate and reactor pres-

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sure (*ca.* 10^{-8} Torr), the B_4H_8CO and B_5H_{11} samples were distilled from a methylcyclohexane slush ($-126°$) directly into the baffled[41] stainless steel or molybdenum Knudsen cell (reactor) of the mass spectrometer. A toluene ($-95°$) slush was used for B_5H_9. The original sample as well as any intermediates and products formed during a pyrolysis could be sampled directly by means of a molecular beam entering the ion source from either a 0.92- or 14.3-mm² orifice in the reactor top. Flow times through the reactor were calculated to be 2.5 or 40 msec, respectively.[15]

The molecular beam was ionized by 70-eV electrons as previously described so that only ions from those neutrals that have had zero ion source contact were identified and measured.[15,40] The ions were accelerated through a 4-kV potential, and mass analyzed in a single-focusing, 12-in. radius of curvature, 60° magnetic deflection analyzer. No ion source magnet was used to collimate the ionizing electrons. Mass peaks were selected by varying the magnetic field ("magnet scanning"). This is intended to minimize mass discrimination effects. By contrast most conventional instruments have source magnets, and the widely used (see below) Consolidated 21-102, 103 series are 180° sector instruments with the source immersed in the magnetic field and with accelerating voltage mass scan.

The sorted ions were detected by a 50% transmission grid or accelerated through an additional potential of 3–4 kV, and detected by a 16- or 20-stage Cu–Be secondary electron multiplier.

The ion current readings could be simultaneously read on a strip chart recorder and an X-Y recorder or, in later experiments, into a PDP-8/S digital computer which was used to calculate the total ion current, molecular beam current grid current, multiplier current, percentage shutter effect,[42] and the multiplier gain. The results were simultaneously stored in the computer's core, printed out on a Teletype, and punched on paper tape for further processing by the university's computer facility.

Appearance potentials were measured by the vanishing current technique from ionization efficiency curves plotted automatically by the X-Y recorder.[43] Argon gas, leaked into the mass spectrometer, was used as the calibrant.

Data and Results

Ions and their neutral progenitors were identified by their mass to charge ratio, mass defect, isotope ratios, "shutter effect,"[42] temperature dependence, and dependence on inlet valve settings. In discussing the mass spectra, only the molecular beam portion of the ion intensity at each mass peak is considered.

Although all the mass spectra reported here are molecular beam mass spectra, that taken at the lowest reactor temperature obtainable (currently room temperature) is called "the molecular beam mass spectrum" if the spectrum is free of contributions from impurities and if evidence for pyrolysis is obtained only after a substantial increase in reactor temperature. This is to be compared with what we call a "conventional" spectrum in which a gas or the efflux from a solids-introduction-probe is admitted to an ion source thermostated at some high temperature, usually *ca.* 250°.

(41) J. Berkowitz, *J. Chem. Phys.*, **36**, 2533 (1962).

(42) The movable beam defining slit ("shutter") located between the reactor orifice and the ion source permitted differentiation of species originating from the reactor, the crucible lip, the radiation shields, and the residual background gases. The ratio of molecular beam to total ion intensity at a given mass peak is called the "percentage shutter effect." Highly reactive species, which are expected to be destroyed by every collision with the vacuum chamber walls, have high per cent shutter effects (~100%), while stable species have small ones (*e.g.*, 5–10% for Ar at these temperatures).

(43) R. J. Loyd and F. E. Stafford, Advances in Chemistry Series, No. 72, American Chemical Society, Washington, D. C., 1967, p 127.
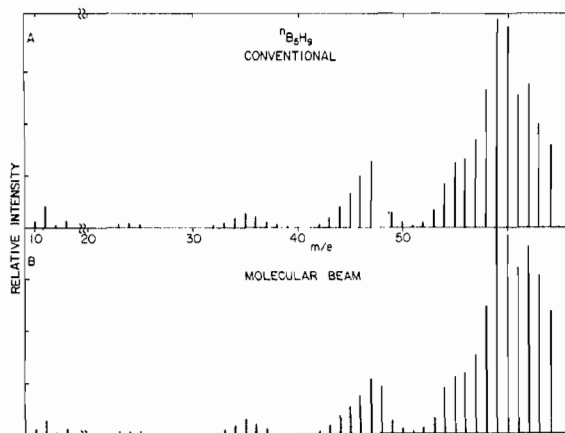
Figure 1.—Pentaborane(9), $^nB_5H_9$, mass spectrum using samples with naturally occurring isotopic distribution. A. Conventional instrument mass spectrum from Quayle[44] (Metropolitan-Vickers M.S. 2, 90° sector, magnetic scanning; source temperature not specified). See Quayle's article for comparison with a spectrum taken with a 180°, accelerating voltage scanning spectrometer. B. Molecular beam mass spectrum from the present work; run 670811.

Consequently, this ion source can give a reproducible and difficult to identify spectrum of a mixture of sample, reactive intermediates, and/or pyrolysis products. This may some times be discerned by variation of the ion source temperature, or by other means; for instance, see ref 24.

In the B_5H_9 study, the normal (20% ^{10}B and 80% ^{11}B) polyisotopic sample was used. In order to simplify the data from the B_4H_8CO and B_5H_{11} studies, samples containing a minimum enrichment of 96% ^{10}B (maximum 4% ^{11}B) were employed.[29] Unless otherwise noted, the data presented below are for these polyisotopic samples.

A. Pentaborane(9).[28]—A preliminary study of pentaborane(9) was carried out in an effort to obtain its molecular beam mass spectrum, and to identify any volatile reactive intermediates and products formed during the pyrolysis. The 14.3-mm² orifice (2.3-msec contact time) was employed for the room-temperature mass spectrum and the 0.92-mm² orifice (40-msec contact time) for the pyrolysis runs.

Pentaborane(9) Molecular Beam Mass Spectrum.— Figure 1 presents the molecular beam mass spectrum of $^nB_5H_9$ taken with a "conventional" ion source instrument[44] compared to that of the molecular beam instrument (see the caption of Figure 1 for spectrometer details). There are no significant differences between the two mass spectra as expected since pentaborane(9) is the most stable[4-6] member of the lower boron hydrides and also is not observed to pyrolyze in our flow reactor (see below). Any differences observed between the molecular beam and conventional mass spectra most probably reflect differences in instrumental characteristics such as variation of multiplier gain with m/e and repeller voltage.

(44) A. Quayle, *J. Appl. Chem.*, **9**, 395 (1959); see also V. Dibeler, F. L. Mohler, L. Williamson, and R. M. Reese, *J. Res. Nat. Bur. Stand.*, **43**, 97 (1949), where a Consolidated 21-102, 180° sector spectrometer with voltage scanning was used.
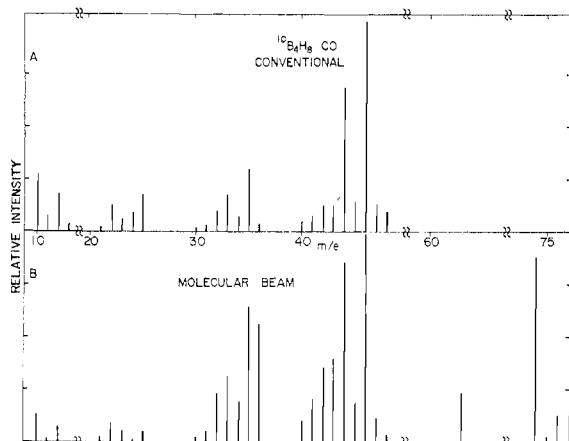
Figure 2.—Calculated monoisotopic mass spectra of $^{10}B_4H_8CO$. A. Conventional mass spectrum (Consolidated Model 21-620 cycloidal mass spectrometer) from data taken by Brennan,[13] with B_5H_x impurity peaks subtracted out. B. Molecular beam mass spectrum; run 680729.

Pentaborane(9) Pyrolysis Mass Spectra.—With a constant flow of $^nB_5H_9$ into the reactor, the ion intensities were studied as a function of reactor temperature. Since this was a preliminary study, only selected peaks were monitored. These were: m/e 11 and 13, representing the monoborane (BH_x^+) ion group; 24 and 27, diborane $(B_2H_x^+)$ group; 35 and 37, triborane $(B_3H_x^+)$ group; 46–48, tetraborane $(B_4H_x^+)$ group; 50 and 52, the $^{11}B_4H_6^+$ and $^{11}B_4H_8^+$ ions, which are important ions in the B_4H_8 mass spectrum (discussed below for B_4H_8CO); 60, 62, and 64, major peaks in pentaborane(9) and -(11) polyisotopic mass spectra; and 65 $(^{11}B_5H_{10}^+?)$, a peak to detect any formation of pentaborane(11). During this pyrolysis, occasional sweeps were made of the higher mass regions to detect any formation of higher boron hydrides.

The temperatures investigated and the absolute intensities of the base peak m/e 59 were: 20° (766 mV); 200° (689 mV); 300° (123 mV); 400° (0.58 mV); 500° (0.57 mV); 600° (0.35 mV).

This partial mass spectrum of pentaborane(9) exhibited no clear trends from 20 to 300°; above 300° the ion intensities dropped sharply, and slight changes in the fragmentation pattern occurred. However, there were no changes in these mass spectra[28] comparable to those observed in the pyrolyses of tetraborane carbonyl and pentaborane(11). Thus, there was no evidence for formation of reactive intermediates, pyrolysis products, nor higher boron hydrides. Any variations in the B_5H_9 pyrolysis spectra above 300° probably are due to experimental errors involved in the measurements of the low ion intensities and to thermally induced variations in the fragmentation pattern.

B. Tetraborane Carbonyl.[28] $^{10}B_4H_8CO$ **Molecular Beam Mass Spectrum.**—The mass spectrum of $^{10}B_4$-H_8CO with the reactor at room temperature differed significantly from that produced by an analytical instrument with the conventional ion source[13] as shown in Figure 2. The latter mass spectrum exhibits no

peaks above mass peak 48 $(^{10}B_4H_8^+)$ after small contributions attributed to pentaboranes have been subtracted; pentaborane(11) is the most likely impurity in the sample.

In the molecular beam mass spectrum, mass peaks 63 and the group 74, 75, and 76 are intense. These peaks are unambiguously assigned to the ions $^{10}B_3H_5CO^+$ (63^+), $^{10}B_4H_6CO^+$ (74^+), $^{10}B_4H_7CO^+$ (75^+), and the parent ion $^{10}B_4H_8CO^+$ (76^+). That B_4H_8CO is completely pyrolyzed in the conventional ion source maintained at $\sim250°$ (as was originally surmised[13]) is confirmed by the absence of mass peaks 63 and 74–76 in Figure 2A.

Noteworthy are the relatively high ion intensities of the $B_4H_xCO^+$ peaks and of the $B_3H_5CO^+$ which can be considered a derivative of B_3H_7. The bulk of the ion intensity, however is distributed among ions containing no CO group. These results parallel the chemical studies[30] of B_4H_8CO in which are observed dissociations of the types: (a) $B_4H_8CO \rightarrow B_4H_8 + CO$; (b) $B_4H_8CO \rightarrow B_3H_5CO + BH_3$. Most of the observed chemical reactions suggest the dissociation found in (a). There is, however, tenuous evidence for the additional dissociation given by (b). The presence of $B_3H_5CO^+$ in the room-temperature molecular beam mass spectrum of B_4H_8CO corroborates the chemical evidence for (b). Other than the ions mentioned, no other carbonyl ions, except CO^+, could be definitely assigned in the tetraborane carbonyl mass spectra.

Depending upon the history of a particular sample, small peaks attributed to the pentaboranes could be identified. Subtracting out the B_5H_{11} molecular beam mass spectrum (see below and ref 28) revealed contributions from smaller amounts of B_5H_9 impurity which were subsequently subtracted out.

No metastable ion peaks were observed for tetraborane carbonyl. Peaks at half-masses, due to the doubly charged ions $^{10}B_4H_3^{2+}$ and $^{10}B_4H_5^{2+}$, were seen at m/e 21.5 and 22.5. These ion intensities were less than 1% of those of the major peaks.

Appearance potentials for the major peaks due to tetraborane carbonyl were measured with the reactor at 20°. This particular sample contained small amounts of pentaboranes. In addition, an appearance potential of the $B_4H_8^+$ ion was taken at 225°. These results are given in Table I.

Temperature Variations.—With a constant flow of B_4H_8CO into the reactor, the decrease in peak heights corresponding to tetraborane carbonyl, the intensities of the other ion peaks, and the changes in the ratios of the various peak heights were studied as a function of reactor temperature. All mass peaks up to 78 were scrutinized, and a few mass peaks beyond 78 were examined for possible formation of higher boranes.

The pyrolysis studies were carried out over a period of 3 years, during which time the electron multiplier was changed from a 16- to 20- stage unit with a corresponding dynode string voltage change from 3.9 to 3.2 kV. The reactor was constructed of stainless steel

Table I
$^{10}B_4H_8CO$ Appearance Potential Data
with the Reactor at 20°

Ion	m/e	AP, eV	Ion	m/e	AP, eV
^{10}B	10	21.8 ± 1	$^{10}B_4H_4$	44	12.6 ± 0.3
$^{10}BH_2$	12	15.3 ± 0.5	$^{10}B_4H_5$	45	13.4 ± 0.4
			$^{10}B_4H_6$	46	11.2 ± 0.2
$^{10}B_2H_2$	22	14.8 ± 0.8	$^{10}B_4H_7$	47	11.5 ± 0.5
$^{10}B_2H_5$	25	12.4 ± 0.8	$^{10}B_4H_8$	48	10.6 ± 0.5
$^{10}B_3H_2$	32	16.7 ± 1	$^{10}B_5H_5$	55	12.5 ± 0.5
$^{10}B_3H_3$	33	14.8 ± 0.5	$^{10}B_5H_7$	57	11.4 ± 0.5
$^{10}B_3H_4$	34	14.3 ± 0.2	$^{10}B_5H_9$	59	10.5 ± 0.5
$^{10}B_3H_5$	35	12.2 ± 0.2			
$^{10}B_3H_6$	36	10.7 ± 0.5	$^{10}B_3H_5CO$	63	11.5 ± 0.5
$^{10}B_3H_7$	37	11.5 ± 0.5			
			$^{10}B_4H_6CO$	74	10.3 ± 0.3
$^{10}B_4$	40	15.9 ± 1	$^{10}B_4H_7CO$	75	10.5 ± 0.5
$^{10}B_4H$	41	13.0 ± 0.8	$^{10}B_4H_8CO$	76	10.2 ± 0.5
$^{10}B_4H_2$	42	13.1 ± 0.8			
$^{10}B_4H_3$	43	12.6 ± 1	$^{10}B_4H_8$	48^a	10.19 ± 0.5

^{a} At 225°.

in the earlier runs and later constructed of molybdenum. However, these changes did not affect the reproducibility of the results. The pyrolysis runs were performed on four separate occasions to verify the reproducibility of the data; measurement of a single mass spectrum at a given temperature and inlet pressure usually required 5–7 hr and included frequent remeasurement of a reference peak to verify that the sample pressures and source conditions remained constant. The initial two pyrolysis runs were made with the 0.92-mm² reactor orifice, the last two with the 14.3-mm² orifice. The larger orifice required higher temperatures to cause complete decomposition of the sample; otherwise the results from the two sets of pyrolysis runs were consistent with one another and gave B_4H_8 mass spectra that were identical within experimental error.

In the mass region 70 to 78, only peaks 74, 75, and 76 were intense. The intensities of these peaks ($^{10}B_4H_xCO^+$ ions) remained constant relative to each other throughout the pyrolysis runs and are assumed to come only from neutral tetraborane carbonyl molecules. These mass peaks are therefore a direct measure of the undecomposed carbonyl leaving the reactor. Peaks 74, 75, and 76 disappeared ($<0.1\%$) at 225° with the 0.92-mm² orifice and at 290° with the 14.3-mm² orifice. Figure 3 shows the temperature variation of mass peak 74 obtained using the 14.3-mm² orifice (2.6-msec nominal contact time).

Higher Borane Formation.—There was no evidence for hexaborane or higher borane formation at any of the temperatures investigated (20–350°) using either of the reactor orifices (detectability limit was 0.1% of base peak at room temperature).

In the mass region 60–69, only peaks 63 and 64 were intense, and they followed the same temperature behavior as the $B_4H_xCO^+$ ions. The ratio of the ion intensities $I(63^+)/I(64^+)$ varied from 6.0 to 9.7 in the pyrolysis runs. This is in reasonable agreement with the calculated value of 8.00 for the ratio of $I(^{10}B_3$-
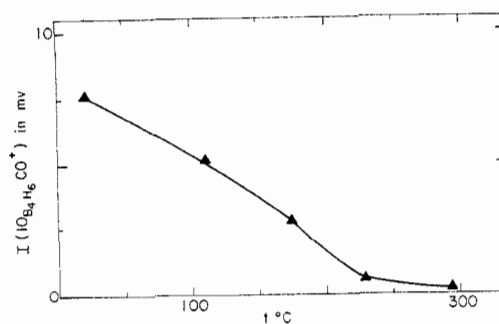

Figure 3.—Pyrolysis of B_4H_8CO: absolute intensity of mass peak 74 ($^{10}B_4H_6CO^+$) as a function of reactor temperature; run 660105 and 2.6-msec nominal contact time.

$H_5CO^+)/I(^{10}B_2{}^{11}BH_5CO^+)$ for a random isotopic distribution in a sample containing the minimum enrichment[29] of 96% ^{10}B.

$B_5H_x{}^+$ **Ions.**—Some samples of tetraborane carbonyl contained small amounts of pentaborane impurities at the beginning of a run. One particular sample showed no observable amounts of pentaboranes with the reactor at room temperature. At 185°, with the smaller (0.92-mm²) orifice, $\Sigma I(B_4H_x{}^+)$ decreased from 59.3 to 38.5, and $\Sigma I(B_5H_x{}^+)/\Sigma I(B_4H_x{}^+)$ increased to 0.092. (See run 650909 of ref 28.)

In a later run (651022) also employing the smaller orifice, the mass spectrum of the sample contained small amounts of pentaborane ions at room temperature. As the reactor temperature was raised the $B_5H_x{}^+$ peaks increased in absolute intensity, but their intensities relative to most of the other mass peaks decreased. Although the $B_5H_x{}^+$ peaks generally exhibited a different temperature dependence than the $B_4H_x{}^+$ peaks, they were sufficiently intense to indicate that fragmentation of pentaborane neutrals could affect the behavior of the B_4H^+, $B_4H_2{}^+$, $B_4H_3{}^+$, and $B_4H_4{}^+$ peaks.

When the larger (14.3-mm²) reactor orifice was employed (660105),[28] however, the $B_5H_x{}^+$ peaks initially present decreased with increasing temperature. This relative decrease in pentaborane formation was due probably to the shorter contact time and lower pressure within the reactor.

$B_4H_x{}^+$ **Ions.**—With the 0.92-mm² orifice (40-msec contact time), mass peak 46 ($^{10}B_4H_6{}^+$) was the major peak (excluding CO^+) below 75°. Above 75° mass peak 44 ($^{10}B_4H_4{}^+$) become the major peak. The ratio of $I(44^+)/I(46^+)$ increased from 0.8 to 20° to 2.2 at 275° where B_4H_8CO was more than 99% decomposed as measured by the intensities of the $B_4H_{6-8}CO^+$ ions.

With the 14.3-mm² orifice (2.6 msec), mass peak 46 was the major peak below 110°, and mass peak 44 was major above 110°. In all of the pyrolysis runs mass peak 46 generally decreased in absolute intensity, whereas mass peak 44 increased with temperature. At 230°, where B_4H_8CO was more than 90% decomposed, mass peak 46 had dropped to 35% of its original absolute intensity. At the same temperature mass peak 44 had dropped to only 83% of its original absolute intesity; *i.e.*, the ratio of $I(44^+)/$
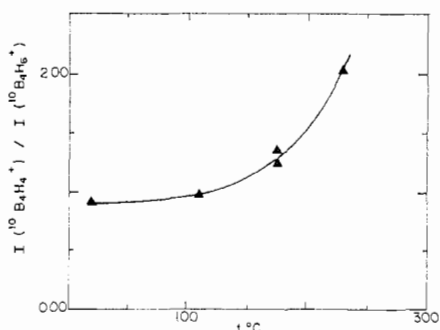
Figure 4.—Formation of B_4H_8 from B_4H_8CO: intensity of mass peak 44 ($^{10}B_4H_4{}^+$) relative to peak 46 ($^{10}B_4H_6{}^+$) as a function of reactor temperature; run 660105.
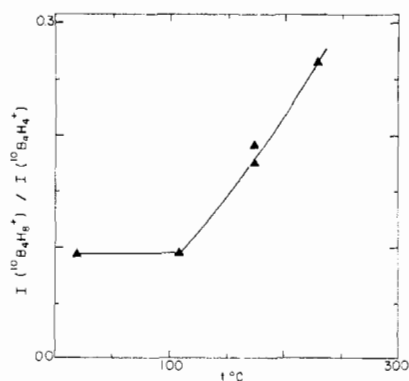

Figure 5.—Formation of B_4H_8 from B_4H_8CO: intensity of mass peak 48 ($^{10}B_4H_8{}^+$) relative to peak 44 ($^{10}B_4H_4{}^+$) as a function of reactor temperature; run 660105.
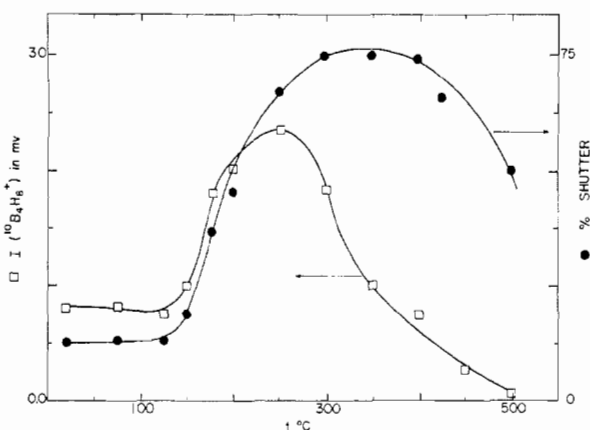

Figure 6.—Formation of B_4H_8: absolute intensity (■) and percentage shutter effect (●) of mass peak 48 ($^{10}B_4H_8{}^+$) as a function of reactor temperature; run 651231.

$I(46^+)$ changed from 0.9 at 20° to 2.0 at 230° (run 660105, ref 28). Since the overall $B_5H_x{}^+$ ion intensities at this temperature were only 15% as great as those of the $B_4H_x{}^+$ peaks, fragmentation of the known pentaborane neutrals could not account for these results. Figure 4 shows the variation of $I(44^+)/I(46^+)$ as a function of temperature and is indicative of the formation of B_4H_8.

The ratio of $I(48^+)/I(49^+)$ varied from 7.0 to 9.3 throughout all the pyrolysis runs. This can be compared to the value of 6.0 calculated for the random isotopic distribution[29] of $I(^{10}B_4H_8{}^+)/I(^{10}B_3{}^{11}BH_8{}^+)$.
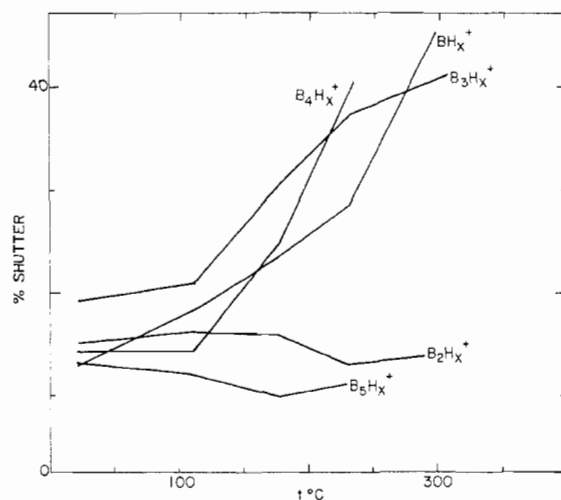

Figure 7.—Pyrolysis of B_4H_8CO: average percentage shutter effects for the major ion groups of B_4H_8CO as a function of reactor temperature; run 660105.

Mass peak 48, which corresponds to the parent peak of B_4H_8 neutral, displayed a significant variation with temperature. In all the pyrolysis runs, the intensity relative to all the major peaks increased steadily up to 230° and higher until general decomposition to solids and hydrogen occurred. The temperature variation of mass peak 48 relative to 44 is illustrated in Figure 5.

Figure 6 shows the variation of the absolute intensity and of the percentage shutter effect (*i.e.*, the fraction of the total ion intensity due to the molecular beam species) for mass peak 48 with temperature. A reactive species such as B_4H_8 would not be expected to form a stable background because it should be rapidly consumed by reaction on or with the vacuum chamber walls. Therefore, ions originating from this molecule are expected to exhibit larger percentage shutter effects than those originating from neutral tetraborane carbonyl or other species. As illustrated in Figure 6, employing the 14.3-mm² orifice, the percentage shutter effect increases from 12% at 20° to 75% at 300–400°; the maximum absolute intensity occurs at 250° (run 651231, ref 28).

In all the pyrolysis runs the percentage shutter effects for the $BH_x{}^+$, $B_3H_x{}^+$, and $B_4H_x{}^+$ ions increase above 20° as shown in Figure 7. The $B_2H_x{}^+$ and $B_5H_x{}^+$ ions do not display these increases in percentage shutter effects; this is due probably to the presence and formation of diborane and pentaborane neutrals, as discussed below.

All the data and results given up to this point strongly suggest the formation of neutral B_4H_8 with mass peak 44 as the major peak in its mass spectrum. To examine this further, with the reactor at room temperature, the ionizing voltage of the $B_4H_8{}^+$ peak was lowered to slightly above the appearance potential of the ion. At 20° there was no observable molecular beam ion current. The reactor temperature was then raised. Above 150°, molecular beam ion current was observable. The results are presented in Table II

TABLE II

FORMATION OF B_4H_8 OBSERVED AT
LOW IONIZING ELECTRON ENERGY

Temp, °C	$I(48^+)^a$	% shutter
Run 651104-40 (0.92-mm² orifice)		
27	0	0
125	0.037	51
225	0.127	88
Run 660110-26 (14.3-mm² orifice)		
20	0	0
150	0.0086	71
250	0.0107	84

^{a} One unit corresponds to about 10^{-16}-A ion current.

and give additional evidence for the appearance of B_4H_8.

In another run (0.92-mm² orifice) the appearance potential of the $B_4H_8^+$ ion at 225° was measured to be 10.2 ± 0.5 eV. This can be compared to the value of 10.4 eV obtained for the $B_4H_8^+$ ion when B_4H_{10} was admitted to the ion source of a conventional instrument.[45] For such conditions, later evidence[22,25] is that the mass spectrum is in fact due to a mixture of B_4H_{10}, B_4H_8, and B_2H_6. The agreement between appearance potentials supports this conclusion, but future work is indicated, particularly in the study of B_4H_{10} appearance potentials under molecular beam conditions.

BH_x^+ and $B_3H_x^+$ Ions.—The mono- and triborane ions generally followed the same temperature behavior as the tetraborane ions. Their behavior showed no indication of the formation of any neutral monoborane or triborane species from tetraborane carbonyl.

$B_2H_x^+$ Ions.—On the whole, the diborane peaks decreased in absolute and relative intensities. However, their percentage shutter effects remained constant and small (10–20%) as compared to the mono-, tri-, and tetraborane ions (about 40% at 230°). This implies the presence of diborane, since diborane forms a stable background in the furnace and ion source chambers.[15] Other tetraborane carbonyl samples, in which the smaller, 0.92-mm² reactor orifice was employed, definitely showed the formation of diborane. Previous work listed diborane as one of the pyrolysis products formed from tetraborane carbonyl.[30]

The percentage shutter effects of the $B_5H_x^+$ ions also were quite small (15%) and remained constant with increasing temperature as illustrated in Figure 7. This is another indication of the presence of pentaboranes.

Mass Spectrum of B_4H_8.—Figure 8 presents a mass spectrum taken with the reactor at 230°, where measurement of the parent $B_4H_xCO^+$ peaks reveals tetraborane carbonyl to be 95% decomposed. The mass spectral contributions of the pentaboranes and undecomposed carbonyl have been subtracted out. Any contributions due to diborane cannot be subtracted since there is no peak that can be attributed only to B_2H_8. The temperature range of 175 to 250° seems to offer the optimum conditions for B_4H_8 formation
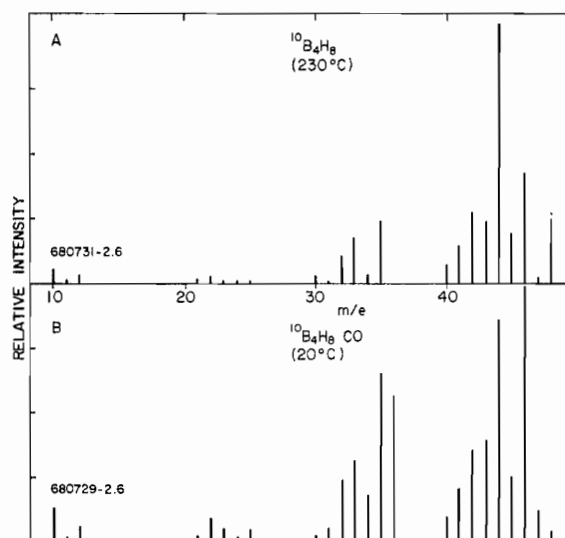

Figure 8.—Calculated monoisotopic molecular beam mass spectra of B_4H_8 and B_4H_8CO. A. Mass spectrum of B_4H_8 formed from B_4H_8CO with the reactor at 230°; run 680731. Contributions from pentaboranes and undecomposed carbonyl have been subtracted out. B. Partial mass spectrum of B_4H_8-CO at 20°; run 680729. Peaks above $B_4H_8^+$ are not included.

under these low-pressure flow conditions (14.3-mm² orifice).

A comparison of the tetraborane(8) mass spectrum with the room-temperature mass spectrum of tetraborane carbonyl in Figure 8B reveals some important differences in the fragmentation patterns. The $B_4H_4^+$ ion (44+) has the largest ion intensity in the B_4H_8 mass spectrum, whereas the $B_4H_6^+$ ion (46+) is the largest for B_4H_8CO (and for B_4H_{10}[22]). The $B_4H_8^+$ ion (48+) has a considerably larger relative intensity for B_4H_8 than for B_4H_8CO or for B_4H_{10}.[22] The ion intensities of the mono-, di-, and triborane ions have smaller relative values for B_4H_8 than for B_4H_8CO. B_4H_8, therefore, undergoes less fragmentation than B_4H_8CO.

Classification of B_4H_8.—These results would seem contradictory since one might expect a transient, "unstable," reactive intermediate to have greater fragmentation to the lower mass ions and a much smaller parent peak. However, various workers[4,46–48] have classified the boron hydrides into (i) the "stable" B_nH_{n+4} series, which includes B_2H_6, B_4H_8, and B_5H_9, and (ii) the "unstable" B_nH_{n+6} series, which includes B_4H_{10} and B_5H_{11}. Mass spectra of stable boron hydrides should display fragmentation to lower mass ions and a relatively intense parent peak, whereas mass spectra of unstable boron hydrides should display greater fragmentation to lower mass ions and a very small or nonexistent parent ion intensity. Therefore, the observed fragmentation pattern of B_4H_8 confirms its classification as a "stable" boron hydride in spite of its transient existence.

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

(46) J. F. Ditter, J. R. Spielman, and R. E. Williams, *Inorg. Chem.*, **5**, 118 (1966).

(47) J. F. Ditter, F. J. Gerhart, and R. E. Williams, Advances in Chemistry Series, No. 72, American Chemical Society, Washington, D. C., 1967, p 191.

(48) S. J. Steck, G. A. Pressley, Jr., F. E. Stafford, J. Dobson, and R. Schaeffer, *Inorg. Chem.*, **8**, 830 (1969); and paper in preparation.
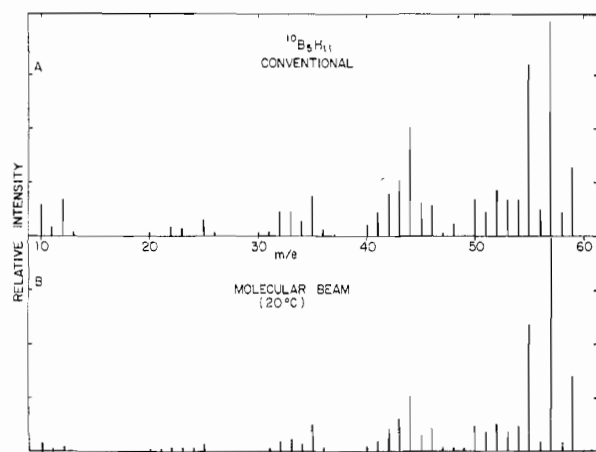
Figure 9.—Calculated ^{10}B monoisotopic mass spectra of pentaborane(11). A. Spectrum from conventional instrument[23] (Consolidated 21-103 B; 180° sector; ion-accelerating voltage mass scan; ion source temperature 270°). B. Molecular beam mass spectrum; run 680919.
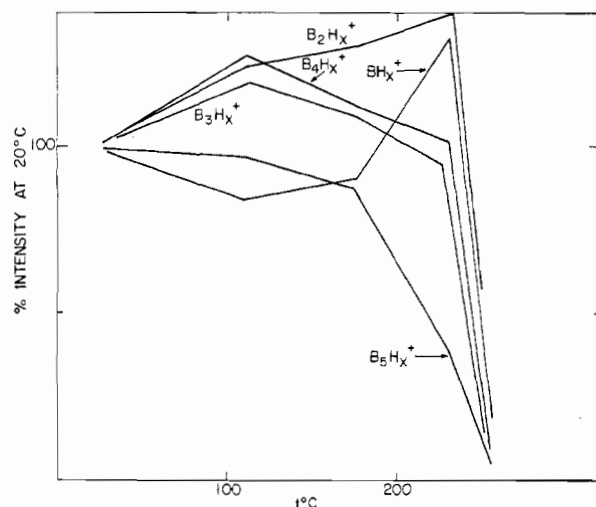

Figure 10.—Pyrolysis of B_5H_{11}: variation of the summed absolute intensities for each of the $B_2H_x^+$, $B_3H_x^+$, $B_4H_x^+$, and $B_5H_x^+$ ion groups as a function of temperature. The intensity for each group is normalized to that measured with the reactor at 20°: $[\Sigma_x I(B_y H_x^+)]_t / (\Sigma_x I(B_y H_x^+)]_{20°}$ vs. t; cf. Figure 9B.

C. **Pentaborane(11).**[28]—The experimental techniques used in measuring the mass spectra of $^{10}B_5H_{11}$ were identical with those used for $^{10}B_4H_8CO$, except that the larger (14.3-mm²) reactor orifice was employed in all the runs. Pentaborane(11), although considered an "unstable" boron hydride,[4,46-48] was appreciably easier to handle than tetraborane carbonyl. There were no detectable (<0.05%) impurity ions (B_4H_{10} and B_5H_9 were excluded on other grounds (see Experimental Section) nor did any become detectable as the samples aged, as was the case for B_4H_8CO.

$^{10}B_5H_{11}$ **Molecular Beam Mass Spectrum.**—Figure 9 gives the entire monoisotopic mass spectrum of pentaborane(11) taken with a conventional ion source instrument[23] (see the caption of Figure 9 for details) compared with that of the molecular beam instrument. Differences exist, although they are not as great as for tetraborane carbonyl (Figure 2). The conventional

mass spectrum exhibits more ion intensity in the lower mass regions: the ions containing two, three, and four borons are roughly twice as large, while those containing one boron are four times as large as in the molecular beam mass spectrum. The increase in fragmentation is due only partly to discrimination by the secondary electron multiplier used for Figure 9B: the maximum measured ratio of gains for pentaborane ions relative to monoborane ions is 2:1. The remainder of the differences may be due in part to differences in instrumentation: accelerating voltage *vs.* magnetic field mass scanning; 180 *vs.* 60° magnetic sector analyzer; unspecified differences in ion-focusing conditions, such as repeller voltage. The effects of just this ensemble of differences is shown clearly by the comparison made by Quayle[44] for B_5H_9 for which we observe no evidence for pyrolysis to gaseous products and could account for almost all of the differences between Figures 9A and 9B.

Indications of pyrolysis in the source, however, do exist. First, Quayle[44] pointed out that the ratio of mass peaks 61:59, which should be indicative of the relative amounts of the two pentaboranes, is "probably very dependent on ionization chamber temperature." Second, the ions BH_3^+ and $B_4H_8^+$ are sensitive indicators of the respective neutrals; these are too small to be discernible in the molecular beam mass spectrum (Figure 9B) but, within the errors inherent in mass spectroscopy and the isotope-stripping procedures necessary to obtain Figure 9A, are readily observed in the conventional spectrum. Unfortunately, there are no differences in the principal peaks of any ion group, such as 44+ for $^{10}B_4H_8$ *vs.* 46+ for $^{10}B_4H_{10}$ or $^{10}B_4H_8CO$, that could be used to distinguish possible pyrolysis intermediates or products. That pyrolysis does occur in the conventional source is, however, corroborated by the data given below for pyrolysis in the flow reactor.

There were no shutterable mass peaks (<0.05%) beyond m/e 61. Mass peak 61 is an ^{11}B isotope peak of the $B_5H_{10}^+$ and $B_5H_9^+$ ions. Mass peak 60 is primarily an isotope peak of the $B_5H_9^+$ ion; subtraction of the ^{11}B contributions generally left very small residues at peaks 60 and 61 that were less than the experimental error. Therefore we conclude that in the molecular beam mass spectrum of B_5H_{11} there is no discernible parent peak as was seen for B_4H_8CO or B_4H_8.

Temperature Variations.—With a constant flow of B_5H_{11} into the reactor, the decrease in the peak heights corresponding to pentaborane(11), the intensities of the other ion peaks, and the changes in the ratios of the various peak heights were studied as a function of reactor temperature. All mass peaks up to 66 were scrutinized, and a few mass peaks beyond 66 were examined for possible formation of higher boron hydrides. The temperatures investigated were between 20 and 500°. Above 230° there was 95% decomposition, but barely discernible intensity tailed off up to 500°, where there was greater than 99%

decomposition to involatile solids and hydrogen. The pyrolysis runs were performed on three separate occasions to verify the reproducibility of the data; measurement of a single mass spectrum at a given temperature and inlet pressure usually required 4–5 hr.

Higher Borane Formation.—There was no observation of the formation of hexaborane or higher boron hydrides at any of the temperatures investigated. Upper limits for the detectability of ion intensities from these neutrals were less than 0.1% of the reference peak at room temperature.

$B_5H_x{}^+$ **Ions.**—As a whole, the $B_5H_x{}^+$ group of peaks decreased relative to the lower mass peaks in all of the pyrolysis runs as shown in Figures 10 and 11. Mass peak 57 ($^{10}B_5H_7{}^+$) was the major peak below 250°; above this temperature mass peak 55 ($^{10}B_5H_5{}^+$) became the major peak. Other details are given in ref 28.

Figures 12A and B illustrate the pentaborane region of B_5H_{11} with the reactor at 20 and 230° compared to that (Figure 12C) of the calculated monoisotopic molecular beam spectrum of $^nB_5H_9$ taken at 20°. The trend in the fragmentation pattern at higher temperature is toward that of B_5H_9; there is a general increase in the relative intensities of mass peaks 50–55 and 59 and a decrease for mass peaks 57 and 58. The studies of B_5H_9 in this laboratory had shown that its molecular beam mass spectrum undergoes no important change from 20° to well above 600°. Therefore it is concluded that pentaborane(9) is a product in the B_5H_{11} pyrolysis.

$B_4H_x{}^+$ **Ions.**—In all the pyrolysis runs, the tetra-, tri-, di-, and monoborane ion intensities increased relative to the pentaborane ion intensities with temperature as shown in Figures 10 and 11. This indicates the formation of at least one boron hydride with a maximum number of four boron atoms. Above 230° the ion intensities dropped sharply due to a general decomposition into solids and hydrogen. Mass peak 44 ($^{10}B_4H_4{}^+$) had the largest ion intensity among the $B_4H_x{}^+$ group, and mass peak 46 ($^{10}B_4H_6{}^+$) had the second largest ion intensity. These two peaks exhibited no clear trends relative to the sum of the $B_4H_x{}^+$ ion intensities as in the B_4H_8CO pyrolysis. The ratio $I(44^+)/I(46^+)$ increased slightly with temperature.

Mass peak 48 ($^{10}B_4H_8{}^+$), which is the most sensitive indicator of B_4H_8 neutral, was approximately one-tenth as large as peak 44 at 20°. $I(48^+)$ increased in absolute intensity from 20° to ~175°, and exhibited the greatest increase among all the $B_4H_x{}^+$ ions relative to the total intensity of the $B_4H_x{}^+$ ion group.

At 230° where the $\Sigma I(B_5H_x{}^+)$ ions had decreased to 40% of their original absolute intensity at 20°, the $B_4H_x{}^+$ ions retained their original intensities, except for $B_4H_8{}^+$ which always increased. The ratio of $I(48^+)/I(49^+)$ was sensibly constant in all the pyrolysis runs and had an average value of 6.0, which agrees with the calculated value of 6.0 for the random isotopic distribution[29] of $I(^{10}B_4H_8{}^+)/I(^{10}B_3{}^{11}BH_8{}^+)$.

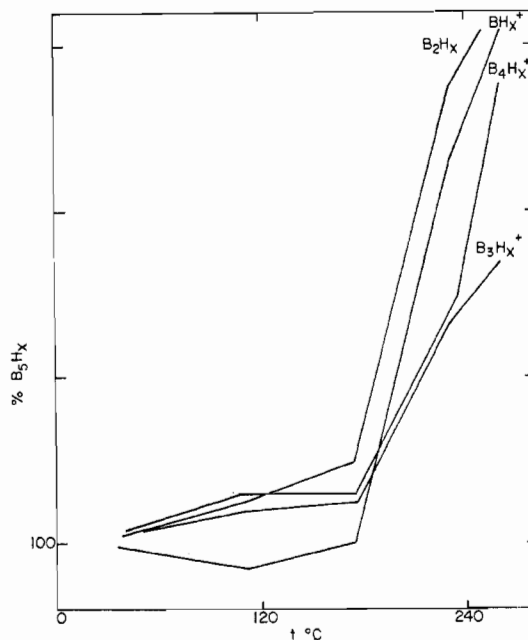Several temperature variation runs were made on

Figure 11.—Pyrolysis of B_5H_{11}: variation with temperature of the total intensities of each of the ion groups containing one, two, three, or four borons relative to the sum for the $B_5H_x{}^+$ group. Each of these ratios is normalized to 100% at 20°. The data are the same as for Figure 10. The increases in these ratios are indicative of the formation of at least one pyrolysis product containing four boron atoms and perhaps lighter boranes also, especially B_2H_6 and BH_3.
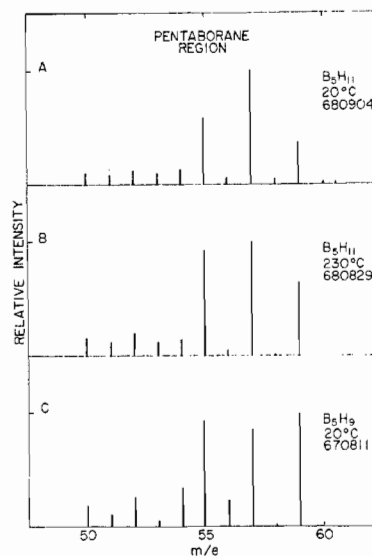

Figure 12.—Calculated monoisotopic mass spectra of the $B_5H_x{}^+$ ions: (A) from B_5H_{11} with the reactor at 20°, run 680904; (B) from B_5H_{11} at 230°, run 680829; (C) from B_5H_9 at 20°, run 670811. The change in spectra from A to B indicates that B_5H_9 is being formed.

the absolute ion intensity and percentage shutter effect of the $B_4H_8{}^+$ ion. A maximum in the absolute intensity occurs at 175°, and the percentage shutter effect increases from 10% at 20° to a maximum of 22% at 225° as illustrated in Figure 13. These results generally duplicate those from B_4H_8CO except the maxima in the absolute intensity and percentage shutter effect are considerably lower for B_5H_{11}. In general
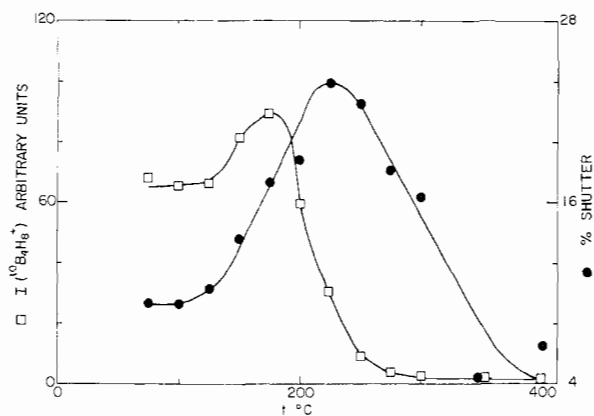
Figure 13.—Formation of B_4H_8 from B_5H_{11}: absolute intensity (squares) and percentage shutter effect (circles) of mass peak 48 ($^{10}B_4H_8{}^+$) as a function of reactor temperature; run 680917.
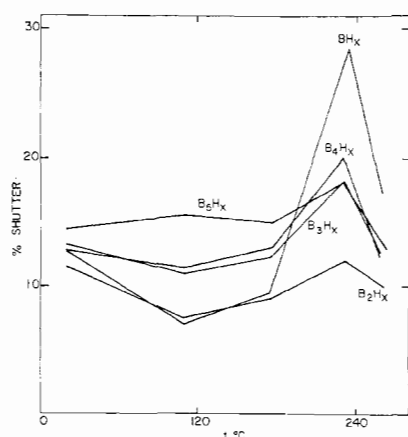

Figure 14.—Average percentage shutter effects for the major ion groups formed from B_5H_{11} as a function of reactor temperature for run 680904.

the percentage shutter effects for all the fragment ion groups from B_5H_{11} increase with reactor temperature, with the $BH_x{}^+$ and $B_4H_x{}^+$ ions exhibiting the greatest increase as illustrated in Figure 14.

Figure 15 gives the calculated monoisotopic mass spectrum of the tetraborane region of B_5H_{11} with the reactor at 20° (Figure 15A) and at 230° (Figure 15B) with the 20° pentaborane spectra subtracted out, compared to the tetraborane region of B_4H_8 taken from tetraborane carbonyl at 230° (Figure 15C). The trend in fragmentation pattern is toward that of B_4H_8. Therefore, it is concluded that the tetraborane species formed in the B_5H_{11} pyrolysis is primarily B_4H_8.

$B_3H_z{}^+$ **Ions.**—In all the pyrolysis runs the triborane ions exhibited the same temperature behavior as the tetraborane ions. The ratio of the $B_3H_z{}^+$ ion intensities to the $B_4H_z{}^+$ intensities varied only from 0.37 at 20° to 0.34 (run 680730[28]) at 230°. The percentage shutter effects increased from 13 to 18% over this temperature range, as compared to a change of 12–20% for the $B_4H_z{}^+$ ions.

The temperature variations of the individual $B_3H_z{}^+$ peaks showed no observable trends. Mass peak 35 ($^{10}B_3H_5{}^+$) had the largest ion intensity in the $B_3H_z{}^+$
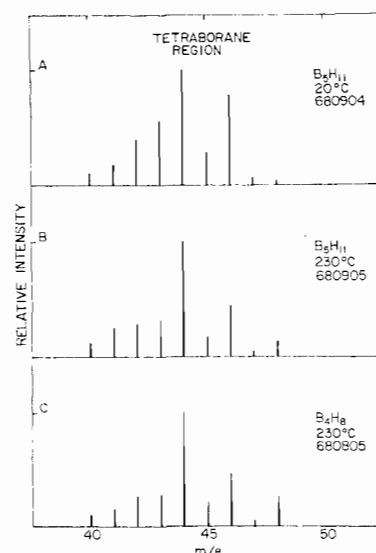

Figure 15.—Calculated monoisotopic mass spectra of the $B_4H_z{}^+$ ions: (A) from B_5H_{11} with the reactor at 20°, run 680904; (B) from B_5H_{11} at 230°, run 680905, with the 20° contributions of pentaborane(9) and -(11) subtracted; (C) from B_4H_8 at 230°, run 680805. The indication is that B_4H_8 is formed from the B_5H_{11}.

group. The ratio $I(35^+)/I(36^+)$ decreased slightly with temperature. Subtraction of the ^{11}B isotopic contributions left no residue at m/e 37, indicating this peak is due only to contributions of the ^{11}B isotopes of the $B_3H_5{}^+$ and $B_3H_6{}^+$ ions. Since B_3H_7 has been previously classified as a "stable" boron hydride,[46–48] one would expect this molecule to exhibit a parent peak as was seen for B_4H_8 (Figure 8A).

Therefore, from the above observations, it is concluded that no neutral triborane species could be discerned as a pyrolysis product of B_5H_{11}.

$B_2H_z{}^+$ **Ions.**—The diborane ions had a different temperature dependence from the other mass peaks in all the pyrolysis runs. The $B_2H_z{}^+$ ion intensities increased relative to the $BH_z{}^+$, $B_3H_z{}^+$, $B_4H_z{}^+$, and $B_5H_z{}^+$ ions from 20 to 230°. The percentage shutter effects of the $B_2H_z{}^+$ ions remained small and constant at 12% between 20 and 230° as shown in Figure 14. This can be contrasted to 29% for the $BH_z{}^+$ ions and 18% for the $B_5H_z{}^+$ ions, at 230°. Diborane forms a more stable background within the ion source and therefore is expected to exhibit lower percentage shutter effects.[15]

Figures 16A and B give the calculated monoisotopic mass spectra of the $B_2H_z{}^+$ region of B_5H_{11} with the reactor at 20 and at 230° where the room-temperature contributions of B_5H_{11} and B_5H_9 have been subtracted out. Figure 16C gives the fragmentation pattern of authentic B_2H_6 at 20°.[15] The $B_2H_z{}^+$ region at 230° is virtually identical with that of diborane itself.

On the basis of the three pieces of evidence, it is concluded that diborane was formed. Previous investigators listed diborane as a major product in the pyrolysis of B_5H_{11}.[49]

(49) A. B. Burg and H. I. Schlesinger, *J. Amer. Chem. Soc.*, **55**, 4009 (1933).

BH_x^+ **Ions.**—The monoborane ion intensities generally followed a different temperature dependence than the other ion groups as shown in Figures 10 and 11. They increased relative to the $B_3H_x^+$, $B_4H_x^+$, and $B_5H_x^+$ ion intensities over the temperature range 20–230°.

The ratio $\Sigma I(BH_x^+)/\Sigma I(B_5H_y^+)$ increased from 0.021 to 0.080 in the temperature range 20–230° for a 280% increase; the ratio $\Sigma I(B_2H_x^+)/\Sigma I(B_5H_y^+)$ increased from 0.026 to 0.096 for a 270% increase (run 680730[28]).

However, the ratio $\Sigma I(BH_x^+)/\Sigma I(B_2H_y^+)$ decreased by 12% from 0.95 to 0.83 implying that the increase in the BH_x^+ ion intensities relative to the $I(B_5H_x^+)$ may be due to the formation and subsequent pyrolytic dissociation of B_2H_6. The formation of B_4H_8 and B_5H_9 also may be contributing to the increase in the BH_x^+ ion intensities. Evidence to the contrary is as follows.

In a previous molecular beam mass spectrometric study of B_2H_6 performed with this apparatus, the maximum ratio of $I(BH_x^+)/I(B_2H_x^+)$ ion intensities was only 0.52 at 652°.[50] These experiments employed a reactor with a flow time of 40 msec (0.92-mm² orifice) *vs.* the 2.6-msec flow time (14.3 mm² orifice) used in these B_5H_{11} studies. Thus in the B_2H_6 studies, the maximum increase in monoborane ion intensity occurred at a much higher temperature and longer flow time than in the present B_5H_{11} pyrolysis. In the B_4H_8 and B_5H_9 molecular beam mass spectra, the ratios $\Sigma I(BH_x^+)/\Sigma I(B_4H_x^+)$ are 0.04 and 0.02, respectively, *vs.* a value of 0.10 for B_5H_{11} at 230°.

Figure 17 presents the calculated monoisotopic mass spectra of the BH_x^+ ion region of B_5H_{11} taken at 20° (Figure 17A) and 230° (Figure 17B) where the 20° contributions of B_5H_{11} and B_5H_9 have been subtracted out compared to the mass spectrum (Figure 17C) of authentic BH_3 formed from B_2H_6 at 500°;[15] spectrum C has been corroborated by work using BH_3CO as the source of BH_3.[19,21] For B_5H_{11}, any contributions due to diborane at 230° have not been subtracted since there is no peak that can be attributed solely to diborane. The trend in the fragmentation pattern from Figure 17A to Figure 17B is toward that of BH_3 as it was in all the pyrolysis runs.

At 230° there is a peak at mass 13 which can be resolved into two components. The lower mass peak is the hydrocarbon peak and it is not shutterable (<0.05%); the higher mass peak is shutterable (50% at 230°). Except for BH_3, no boron hydride has been known to fragment under electron impact ionization to produce a BH_3^+ ion. These data are strong evidence that mass peak 13 is $^{10}BH_3^+$ from BH_3 neutral.

The BH_x^+ ions exhibited the largest percentage shutter effects at higher temperatures as shown in Figure 14. Their percentage shutter effects increased from 13% at 20° to 30% at 230°. The percentage shutter effect for mass peak 13 ($^{11}BH_2^+$ at 20°, $^{10}BH_3^+$ at 230°) increased from 11 to 51%.

Since mass peak 13 was quite small (0.01–1.8% of

(50) E. J. Sinke, M.S. Thesis, Northwestern University, Evanston, Ill., 1965.
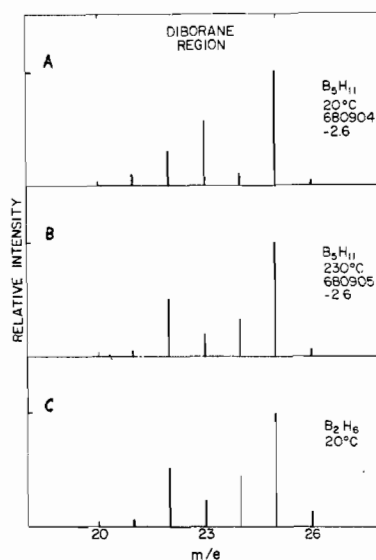

Figure 16.—Calculated monoisotopic mass spectra of the $B_2H_x^+$ ions: (A) from B_5H_{11} with the reactor at 20°, run 680904; (B) from B_5H_{11} at 230°, run 680905, with the 20° contributions of pentaborane(9) and -(11) subtracted; (C) from B_2H_8 at 20°.[15] This indicates formation of diborane.
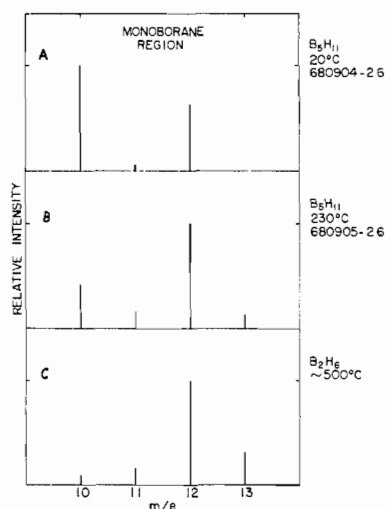

Figure 17.—Calculated monoisotopic mass spectra of the BH_x^+ ions: (A) from B_5H_{11} with the reactor at 20° for run 680904; (B) from B_5H_{11} at 230°, run 680905, with the 20° contributions of pentaborane(9) and -(11) subtracted; (C) from BH_3 at 500°.[15] This indicates formation of BH_3 from B_5H_{11}.

the reference peak), several temperature variation runs were performed on the $^{10}BH_2^+$ ion intensity to observe the behavior of the absolute ion intensity and the percentage shutter effect. As illustrated in Figure 18, a maximum in the percentage shutter effect occurs at 250°, but there is no well-defined maximum in the absolute ion intensity as for the $B_4H_8^+$ ion.

That the observed changes in the BH_x region are due only to fragmentation of heavier pyrolysis products or to pyrolysis of diborane is excluded. The intercomparison of fragmentation patterns and the variation of intensities and shutter per cents of m/e 13 and 12 with temperature can be explained only by the formation of BH_3 neutral from B_5H_{11} during the course of the pyrolysis.
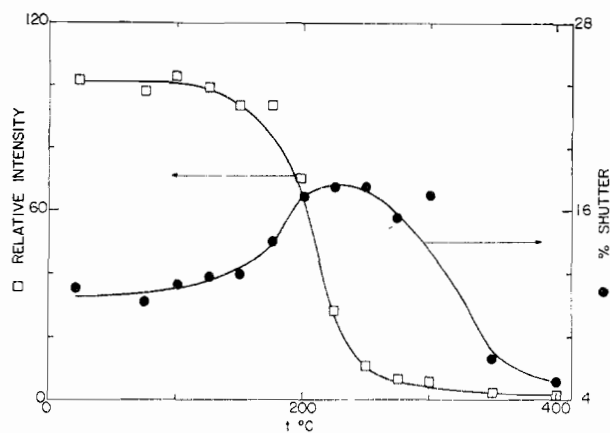
D. Comparison of the Mass Spectrum Produced

Figure 18.—Absolute intensity (squares) and percentage shutter effect (circles) for mass peak 12 ($^{10}BH_2^+$) as a function of reactor temperature. This also indicates formation of BH_3 from B_5H_{11}.
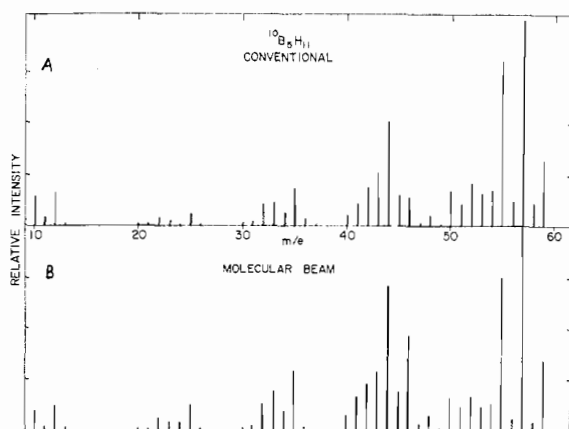

Figure 19.—Calculated ^{10}B monoisotopic mass spectra of pentaborane(11): (A) mass spectra taken with a conventional instrument;[23] (B) molecular beam mass spectrum at 230°, run 680905. *Cf.* Figure 9; the increased similarity of Figures 19A and 19B is evidence for pyrolysis in the source of the "conventional" instrument.

with the Reactor at 230° with the Conventional Mass Spectrum and with that of B_4H_8.—Figure 19A gives the mass spectrum of B_5H_{11} taken with a conventional ion source[23] compared with the calculated monoisotopic mass spectrum produced when B_5H_{11} flows through the reactor at 230° (Figure 19B). This comparison may be contrasted to that made in Figure 9. There is now closer agreement between the molecular beam and the conventional mass spectra. This supports the conclusion reached in the discussion of Figure 9 that the spectrum produced when B_5H_{11} is introduced into the conventional mass spectrometer is actually that of a steady-state mixture of B_5H_{11}, B_5H_9, B_4H_8, B_2H_6, and/or BH_3, with the conventional source acting as a flow reactor.

Figure 20 presents the calculated monoisotopic spectrum obtained when B_5H_{11} is passed through the reactor at 230°, with the contribution from B_5H_9 and B_5H_{11} subtracted out, using their fragmentation patterns at room temperature (Figure 20A), compared to the mass spectrum of B_4H_8 produced from B_4H_8CO (Figure 20B). The most important difference between
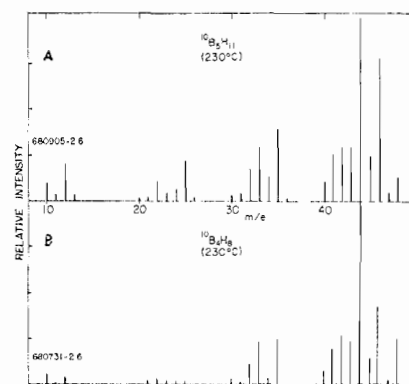

Figure 20.—Calculated monoisotopic mass spectra of pentaborane(11) and B_4H_8: (A) mass spectrum of products from B_5H_{11} at 230°, run 680905, with the contribution from B_5H_{11} and B_5H_9 subtracted out; (B) mass spectrum of B_4H_8 at 230°, run 680731.

Figures 20A and B is that the monoborane ions are twice as intense in Figure 20A as in the B_4H_8 spectrum, thus indicating formation of BH_3. Also the $B_2H_x^+$ ions are larger, indicating formation of B_2H_6. The triborane and tetraborane regions, respectively, are approximately of the same intensity. This is further evidence for the formation of B_4H_8 and BH_3 when B_5H_{11} is pyrolyzed.

Conclusions

A preliminary study of the molecular beam mass spectrum and pyrolysis of pentaborane(9) has shown that its molecular beam mass spectrum exhibits no great changes when the reactor temperature is increased and that there is a general agreement with the conventional spectrum taken with a sector instrument with magnetic mass scanning. These results indicate the B_5H_9 does not decompose to give detectable amounts of volatile boranes under these low-pressure flow conditions.

The (molecular beam) mass spectrum of B_4H_8CO was obtained. The fragmentation pattern shows trends similar to those observed in the chemistry of B_4H_8CO. Pyrolysis of B_4H_8CO is shown to be an efficient source of B_4H_8. There was no evidence for the formation of monoborane or a triborane. Small amounts of pentaboranes and diborane could be observed. No hexaborane or higher boron hydrides were found. From these data a complete mass spectrum of the B_4H_8 intermediate was obtained (Figure 8). The fragmentation pattern of the B_4H_8 molecule confirmed its previous classification[46-48] as a "stable" boron hydride.

The investigation of the pyrolysis of B_5H_{11} has shown that B_5H_{11} dissociates into B_4H_8 and BH_3. The temperature variations of the B_2 and B_5 ions have shown diborane and pentaborane(9) to be additional pyrolysis products. There was no evidence for the formation of a triborane species, nor was there evidence for the formation of higher boron hydrides.

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AEROJET-GENERAL CORPORATION, LOS ANGELES, CALIFORNIA   90007

Direct Synthesis of *closo*-Carboranes

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Pentaborane-9 and acetylene can react in a continuous-flow system to produce directly the smaller *closo*-carboranes $1,5$-$C_2B_3H_5$, $1,6$-$C_2B_4H_6$, and $2,4$-$C_2B_5H_7$ in combined yields approaching 65–70%. Reactions of decaborane-14 with acetylene under the same conditions, excepting a somewhat higher temperature, give predominantly $1,7$-$C_2B_{10}H_{12}$ in yields also on the order of 70%. Optimal conditions for both systems include short residence times ($\sim$0.5 sec), high temperatures (500–600°, depending on the system), a diluent gas, and a steel wool plug or diffuser. The reactions are highly exothermic, and drastic reduction of yields can occur if the heat is not dissipated, as was evident in a scaled-up unit where very careful diluent control had to be exercised to prevent sudden surges to very high temperatures.

Introduction

In a previous publication[2] we reported a high-yield synthesis of the small *closo*-carboranes $1,5$-$C_2B_3H_5$, $1,6$-(and $1,2$-) $C_2B_4H_6$, and $2,4$-$C_2B_5H_7$, with the respective systematic names of *closo*-1,5-dicarbapentaborane-5, *closo*-1,6-dicarbahexaborane-6, and *closo*-2,4-dicarbaheptaborane-7, from the *nido*-carborane, $4,5$-$C_2H_4H_8$. High yields were realized under appropriate short-term, high-temperature, continuous-flow conditions, and yields were nearly quantitative when temperature–time conditions were sufficiently mild to convert only a fraction (25–30%) of the *nido*-carborane reactant to products at one time and provided further that a low pressure, on the order of 10 mm absolute, was maintained. Even at higher temperatures, where no *nido*-carborane survived the treatment, the yield of *closo*-carboranes was still around 60%. Even with these limitations and the further limitation of a maximum yield of 40% in the synthesis of the *nido*-carborane reactant,[3,4] this method of preparing the small *closo*-carboranes represented a significant advance in the state of the art. Previously, except for $C_2B_5H_7$,[3] only trace amounts of these compounds had ever been generated, and these generally *via* silent electric discharge of flashing reactions between boranes and acetylene.[5–10]

In contrast, the icosahedral *closo*-dicarbadodecaborane $1,2$-$C_2B_{10}H_{12}$ has been available in fairly high yields since its discovery.[11] Its synthesis, based on Lewis base solution chemistry, involves multistep procedures,[12] while its rearrangement to the 1,7 compound involves further handling in the form of high-temperature gas-phase pyrolysis.[13,14] Preparation of $1,12$-$C_2B_{10}H_{12}$ involves similar gas-phase pyrolysis of the 1,7 compound.[15]

In our previous paper,[2] preparation of the small *closo*-carboranes required as a first step the synthesis and purification of the *nido*-carborane $4,5$-$C_2B_4H_8$ by long-term reaction between pentaborane-9 and acetylene (48 hr at 215–225°) and as a second step subjection of the *nido*-carborane to short-term, high-temperature conditions to get the *closo*-carboranes. It seemed reasonable, therefore, to try to combine the two steps into one by subjecting the initial reactants, pentaborane-9 and acetylene, to the appropriate short-term, high-temperature conditions and thereby obtain the *closo*-carboranes directly in one step. As will be evident later, this new direct synthesis is not simply an extension of the earlier reaction because, first of all, the *nido*-carborane $C_2B_4H_8$ is not an intermediate here, and secondly the product distribution is significantly different. In addition to the pentaborane-9–

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