$$x\mathrm{Si_2H_6} \xrightarrow{\mathrm{KH}} x\mathrm{SiH_4} + (1/x)(\text{-}\mathrm{SiH_2}\text{-})_x \quad (3)$$

$$(1/x)(\text{-}\mathrm{SiH_2}\text{-})_x + \mathrm{KH} \longrightarrow \mathrm{KSiH_3} \quad (4)$$

The reaction represented by eq 3 is very fast while the reaction represented by eq 4 is slow. A reaction similar to route 4 was also observed in the disilane–lithium hydride reaction.

The decomposition of digermane by potassium hydride is much faster than any of the disilane decompositions. The change in the order of the relative rates with potassium hydride suggests that a different reaction path is followed. Germane does react with potassium hydride to form potassium germyl but not fast enough to account for the rapid appearance of potassium germyl in the digermane–potassium hydride reaction. These results suggest that digermane and potassium hydride may react primarily without going through a polymer (M_xH_{2x+2}, where $x = 3$ or more, M = Si or Ge) as must be the case for disilane with potassium hydride[1]

$$\mathrm{KH} + \mathrm{Ge_2H_6} \longrightarrow \mathrm{KGeH_3} + \mathrm{GeH_4} \quad (5)$$

Thus, the potassium hydride–digermane reaction may be a fairly simple cleavage reaction while the potassium hydride–disilane reaction may involve numerous disproportionation and cleavage reactions in which disilane is regenerated

$$2\mathrm{Si_2H_6} \xrightarrow{\mathrm{KH}} \mathrm{SiH_4} + \mathrm{Si_3H_8} \quad (6)$$

$$\mathrm{Si_3H_8} \xrightarrow{\mathrm{KH}} \mathrm{KSiH_3} + \mathrm{Si_2H_6} \quad (7)$$

$$2\mathrm{Si_3H_8} \xrightarrow{\mathrm{KH}} \mathrm{Si_2H_6} + \mathrm{Si_4H_{10}}, \text{ etc.} \quad (8)$$

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
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Electron Impact Fragmentation of $B_{10}H_8(N_2)_2$ and Isotopic Composition of Decaborane(14)[1]

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The mass spectrum of $B_{10}H_8(N_2)_2$ which has a closed polyhedral boron skeleton was examined and compared with that of decaborane(14) which has an open-faced icosahedral fragment boron skeleton. There is less boron fragmentation from $B_{10}H_8(N_2)_2$ than from $B_{10}H_{14}$. Prominent ions were $B_{10}H_8N_4^+$ and $B_{10}H_8N_2^+$, with no evidence of similar ions with fewer than eight hydrogens. The ion current patterns of these ions were used to determine the per cent of boron-10 in the sample. Overlapping $B_{10}H_x^+$ ion currents were resolved to show large contributions from species with x even and small or negligible contributions for x odd. Appearance potential differences are 0.60 ± 0.05 V for the loss of one N_2 molecule and 1.80 ± 0.05 V for the loss of two N_2 molecules. Metastable ions indicate the reactions $B_{10}H_8N_4^+ \rightarrow B_{10}H_8N_2^+ + N_2$ and $B_{10}H_8N_2^+ \rightarrow B_{10}H_8^+ + N_2$ take place in the spectrometer.

Decaborane, $B_{10}H_{14}$, has an icosahedral fragment skeleton of boron atoms in which the bonding is best described as delocalized or aromatic.[2] Electron impact ionization results in fragmentation favoring loss of H_2 and BH_3 units, to give $B_{10}H_n^+$ ions of greater abundance for n even than for n odd and $B_xH_y^+$ ions in appreciable abundance.[3] Derivatives of the $B_{10}H_{10}^{2-}$ ion have a closed polyhedral boron skeleton in which the bonding is probably completely delocalized ellipsoidally rather than having an open face as in decaborane. Electron impact ionization of 1,10-$B_{10}H_8(N_2)_2$, a relatively volatile derivative of $B_{10}H_{10}^{2-}$,[4] was investigated to determine if the fragmentation processes from a closed polyhedral structure are significantly different from those from the open-faced polyhedral fragment structure of decaborane. In addition, relative ion currents were used to determine the boron isotopic composition.

Results

The natural isotopic composition of boron is about 80% ^{11}B and 20% ^{10}B. For a group of ten borons, $^{11}B_8{}^{10}B_2$ is the most probable isotopic composition, but six others have probabilities greater than 1% of the most probable composition. Table I gives the relative abundances of $B_{10}H_8$ and $B_{10}H_8N_4$ species calculated from often quoted natural abundances of B (19.6% ^{10}B), H (1.5×10^{-2}% ^2H), and N (0.36% ^{15}N), and also from 20.20% ^{10}B and natural abundances of H and N isotopes. Values are changed only in the fourth significant figure by neglecting the effect of ^2H. Similar calculations were performed at 0.10% intervals for ^{10}B from 19.00 to 21.00%. Masses 175, 147, and 119 arise from species containing ^2H or ^{15}N.

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(1) Reported in part at the Second Midwest Regional Meeting of the American Chemical Society, Lawrence, Kans., Oct 1966. Acknowledgment is made to the donors of The Petroleum Research Fund, administered by the American Chemical Society, and to the University of Kansas General Research Fund for partial support of this research.

(2) For a discussion of structures and bonding, see W. N. Lipscomb, "Boron Hydrides," W. A. Benjamin, Inc., New York, N. Y., 1963.

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TABLE I

RELATIVE PROBABILITIES OF ISOTOPIC SPECIES, ASSUMING $1.5 \times 10^{-2}\%$ ^2H AND 0.36% ^{15}N

Mass	19.6% ^{10}B	20.2% ^{10}B
	$B_{10}H_8N_4$	
175	0.58	0.54
174	38.43	35.68
173	91.79	88.42
172	100.00	100.00
171	64.78	67.26
170	27.58	29.73
169	8.06	9.02
168	1.63	1.90
	$B_{10}H_8$	
119	0.045	0.04
118	37.47	34.76
117	91.21	87.84
116	100.00	100.00
115	64.99	67.48
114	27.72	29.89
113	8.11	9.08
112	1.65	1.91

Parent Ions, $B_{10}H_8N_4^+$.—In Table II are given the relative ion currents observed in one run at a nominal ionizing electron potential of 70 V. Spectra obtained at electron potentials less than 4 V above the appearance potential of $B_{10}H_8N_4^+$ yielded less precise but not significantly different relative ion currents. The ratio of any two relative ion currents can be used to calculate the boron isotope ratio. The relative intensities of five peaks give 10 ratios. Abundances of ^{10}B calculated from four runs using the $B_{10}H_8N_4^+$ peaks average 20.2% and are summarized in Table III. If the natural abundance of ^{15}N is not included in the calculations, the calculated abundance of ^{10}B is 20.0%.

TABLE II

RELATIVE ION CURRENTS FROM ELECTRON BOMBARDMENT OF $B_{10}H_8(N_2)_2$

m/e	Relative current base 100 peak, *m/e* 115	Relative current for species
	$B_{10}H_8N_4^+$	
175	0.44	1.0
174	15.5	35.4
173	38.7	88.5
172	43.8	100.0
171	29.3	66.9
170	13.0	29.6
169	3.9	8.8
	$B_{10}H_8N_2^+$	
147	0.31	0.6
146	17.8	34.8
145	44.9	87.8
144	51.1	100.0
143	34.6	67.7
142	15.4	30.1
141	4.9	9.5

$B_{10}H_8N_2^+$ Ions.—In Table II are given relative ion currents observed at an electron potential of 70 V. The same relative ion currents within the range *m/e* 141–147 were obtained at potentials less than 4 V above the appearance potential of $B_{10}H_8N_2^+$. In addition, metastable ions were observed with peaks at *m/e* 122.7, 121.7, 120.6, and 119.6 (calcd for $B_{10}H_8N_4^+ \rightarrow B_{10}H_8N_2^+ + N_2$, m^* 122.5, 121.5, 120.6, 119.6). Isotope abundances calculated from the $B_{10}H_8N_2^+$ ion currents in two runs averaged 20.25% ^{10}B and are summarized in Table III. Neglect of ^{15}N gives the value 20.1% ^{10}B.

TABLE III

DETERMINATION OF BORON ISOTOPIC COMPOSITION, ASSUMING 0.36% ^{15}N

m/e	Electron potential, V	No. of ratios	Av % ^{10}B	Std dev
169–174	75	15	20.2	0.25
170–174	75	10	20.2	0.07
170–174	70	10	20.3	0.2
170–174	5 above AP	10	20.2	0.2
142–146	75	10	20.3	0.05
142–146	70	10	20.2	0.4
$B_{10}H_8N_4^+$		45	20.2	0.2
$B_{10}H_8N_2^+$		20	20.25	0.3
All of the above		65	20.2	0.2

$B_{10}H_x^+$.—At electron potentials close to the appearance potential of *m/e* 118, the relative ion currents of *m/e* 113–118 corresponded to those of *m/e* 169–174 and 141–146. Metastable ions at *m/e* 95.4, 94.5, 93.6, and 92.6 were observed (calcd for $B_{10}H_8N_2^+ \rightarrow B_{10}H_8^+ + N_2$, m^* 95.4, 94.4, 93.4, 92.5). At higher potentials, hydrogen fragmentation occurred giving overlapping $B_{10}H_x^+$ patterns with $0 \leq x \leq 8$. The boron isotopic composition determined from the $B_{10}H_8N_4^+$ and $B_{10}H_8N_2^+$ patterns (20.2% ^{10}B) was used with the 14 intensities at *m/e* 105–118 to determine the amounts of the nine $B_{10}H_x^+$ species ($0 \leq x \leq 8$) by a least-squares analysis. The results from one run are summarized in Table IV. In other runs, similar results were obtained with relative contributions from $B_{10}H_x^+$ of 100 (x = 8), 100 (6), 50 (4), 50 (2), 40 (0), and small (<10) positive or negative contributions from x = 7, 5, 3, and 1.

TABLE IV

RELATIVE ABUNDANCES OF $B_{10}H_x^+$ SPECIES AT 75 EV AND THE CALCULATED SPECTRUM WITH 20.2% ^{10}B AND 0.015% ^2H IN $B_{10}H_8$

Species	Calcd abundance	*m/e*	Intensity	
			Calcd	Obsd
$B_{10}H_8^+$	100	118	21.89	21.8
$B_{10}H_7^+$	−1	117	55.15	55.1
$B_{10}H_6^+$	104	116	85.27	85.0
$B_{10}H_5^+$	2	115	100.00	100.00
$B_{10}H_4^+$	48	114	95.66	95.3
$B_{10}H_3^+$	−4	113	76.66	76.7
$B_{10}H_2^+$	55	112	61.49	61.3
$B_{10}H^+$	9	111	56.80	56.9
B_{10}^+	41	110	57.56	57.1
		109	54.20	54.9
		108	40.50	39.7
		107	22.34	21.8
		106	8.89	9.8
		105	2.55	4.9

Lower Fragment and Double Ions.—Smaller amounts of $B_9H_x^+$ ions were observed at *m/e* 95–104, with a maximum at *m/e* 98, indicative that the average value of x

is considerably less than 8. The total ion current in this region was about 10% of that in the region *m/e* 105–118 ($B_{10}H_x^+$), or about 7% of that above *m/e* 105 ($B_{10}H_x^+$, $B_{10}H_8N_2^+$, $B_{10}H_8N_4^+$). The spectra showed evidence of still smaller amounts of B_8, B_7, and lower fragments complicated by overlap with doubly charged ions. No attempt was made to analyze these last quantitatively because of the low ion currents involved.

Doubly charged ions $B_{10}H_xN_4^{2+}$, $B_{10}H_xN_2^{2+}$, and $B_{10}H_x^{2+}$ also were observed. A rigorous analysis of relative ion currents was not carried out because of overlap with whole-numbered peaks of the lower fragment single ions, but half-integral peaks appeared at low enough *m/e* values to indicate appreciable hydrogen fragmentation from the double ions.

For comparison, the spectrum of decaborane was run under comparable conditions in our instrument.[5] Ion currents in the region *m/e* 95–105 were about 15% of the ion currents for *m/e* 106–124.

Appearance Potentials.—The appearance potential of the parent ion lay between 9 and 10 V but was not determined accurately because plots of the log of the ion current *vs.* apparent voltage were not parallel to those of calibrating gases (Ar, Kr, Hg). However, such plots for $B_{10}H_8N_4^+$, $B_{10}H_8N_2^+$, and $B_{10}H_8^+$ were parallel and the differences between them were reproducible. The differences AP(*m/e* 174) − AP(*m/e* 146) = 0.60 ± 0.05 V and AP(*m/e* 174) − AP(*m/e* 118) = 1.85 ± 0.05 V were obtained from three runs.

Discussion

Fragmentation.—The observation of metastable ions corresponding to the processes $B_{10}H_8N_4^+ \rightarrow B_{10}H_8N_2^+ + N_2$ and $B_{10}H_8N_2^+ \rightarrow B_{10}H_8^+ + N_2$ indicates that the *stepwise* loss of two nitrogen molecules from the parent ion is an important reaction path. In the absence of independent information about ionization potentials or heats of formation of the fragments, their appearance potentials give only single equations in two unknowns, or bond dissociation energies of ions not directly applicable to neutral species. The greater dissociation energy for loss of the second N_2 group from the ion may be indicative of an electronic interaction between substituents in the 1,10 positions or of a reorganization of the B_{10} structure on loss of N_2. Extended Hückel LCAO–MO calculations[6] of $B_{10}H_8(N_2)_2$[7] mix boron "surface" electrons with N_2 π^* orbitals, indicating the stability of the compound is due in part to delocalization of boron "surface" electron density into the N_2 groups. This could be expected to be less when two N_2 groups compete, accounting for the difference between first and second dissociation energies from the ions. It has been suggested that a "resonance" interaction exists between substituents in the 1,10 positions of $B_{10}H_{10}^{2-}$.[8]

The difference in appearance potentials between $B_{10}H_8N_4^+$ and $B_{10}H_8N_2^+$ can be expressed as: AP($B_{10}H_8N_2^+$) − AP($B_{10}H_8N_4^+$) = IP($B_{10}H_8N_2$) − IP($B_{10}H_8N_4$) + D_1(B–N_2), where D_1(B–N_2) is the dissociation energy for the loss of the first N_2 group from neutral $B_{10}H_8(N_2)_2$. In the dissociation, N_2 takes both electrons from the B–N bond, so no electron is left to increase B–B bonding in the fragment ion. That $B_{10}H_8N_2^+ + N_2$ is observed rather than $B_{10}H_8N_2 + N_2^+$ indicates that IP($B_{10}H_8N_2$) is much less than 15.5 V, or IP($B_{10}H_8N_2$) − IP($B_{10}H_8N_4$) $\ll$ 6 V. Quite probably, IP($B_{10}H_8N_2$) is *less than* IP($B_{10}H_8N_4$), so that IP($B_{10}H_8N_2$) − IP($B_{10}H_8N_4$) < 0. Assuming this difference to be 0, −1.0, and −2.0 V gives calculated D_1(B–N_2) values of 14, 37, and 60 kcal/mol, respectively, all much weaker than *D*(B–H) which is about 100 kcal/mol. Using AP($B_{10}H_8^+$) − AP($B_{10}H_8N_4^+$) = IP($B_{10}H_8$) − IP($B_{10}H_8N_4$) + 2*D*(B–N_2) and the assumptions IP($B_{10}H_8$) − IP($B_{10}H_8N_4$) = 0, −1.0, and −2.0 V gives values for the average B–N_2 dissociation energy, $\bar{D}$(B–N_2) = 21, 32, and 44 kcal/mol. The assumption that the ionization potential differences lie in the quoted ranges is supported by extended Hückel calculations performed by us which predict IP($B_{10}H_8$) − IP($B_{10}H_8(N_2)_2$) = −1.0 V. Previous experience with such calculations has shown that trends are reliable and absolute values are usually off by a constant factor of 2 or less. Only if the loss of N_2 is accompanied by a boron cage rearrangement to a much stabler structure could $\bar{D}$(B–N_2) reasonably be larger than 50 kcal/mol.

The greater relative abundance of $B_9H_x^+$ ions from $B_{10}H_{14}$ than from $B_{10}H_8(N_2)_2$ is to be expected from the larger H to B ratio of $B_{10}H_{14}$ and from its structure. The bridging hydrogens attached to B(6) and B(9) would facilitate the loss of B as stabler BH_2 or BH_3 units rather than as B or BH units which one would expect from $B_{10}H_8(N_2)_2$ in which no boron is bonded to more than one hydrogen.

The larger relative abundance of $B_{10}H_x^+$ ions with *x* even than with *x* odd is undoubtedly due to the preferential loss of stable H_2 molecules rather than separate atoms.

Isotopic Composition.—The invariance of the relative ion currents within the ranges *m/e* 168–174 and 140–146 over a wide range of ionizing electron energies is in contrast to the changing pattern at *m/e* 118 and below and to the changing spectrum of $B_{10}H_{14}$. This is indicative that, in the former two ranges, no hydrogen fragmentation occurs and only $B_{10}H_8N_4^+$ and $B_{10}H_8N_2^+$ ions are observed, permitting the boron isotopic composition to be calculated. The isotopic composition determined here (20.2% ^{10}B) is consistent with a previously observed enrichment in ^{10}B occurring in the synthesis of boranes from "normal" borax,[9] most likely owing to a boron kinetic isotope effect.

When ^2H and ^{15}N are assumed to be absent, the calculated abundance of ^{10}B is slightly lower than when natural abundances of ^2H and ^{15}N are assumed. Although the observed ion currents at *m/e* 175, 147, and

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[5] Ion currents from fragments containing fewer than ten borons were qualitatively similar but a smaller fraction of the ten-boron ions than were reported in a study of the mass spectrum of monoisotopic decaborane, $^{11}B_{10}H_{14}$.[8]

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119 were slightly larger than theoretical for natural abundances, they were on the same order of magnitude as the background currents, because of the relatively low sample pressures used (*ca.* 10^{-6} torr) and so cannot be regarded as very accurate. They are indicative that neglect of ^2H and ^{15}N could give just barely significant differences in the calculated ^{10}B abundances and that the abundances of ^2H and ^{15}N are not significantly different (to determination of ^{10}B abundance) from natural abundances. They are also indicative that ion–molecule reactions leading to $B_{10}H_9N_4^+$, etc., must be negligible under these conditions.

With ordinary laboratory chemicals and equipment, decaborane can be converted to $B_{10}H_8(N_2)_2$, the mass spectrum of which yields many more parameters than are necessary for the determination of the boron isotopic composition, without the complication of overlapping hydrogen fragmentation that is present in the spectrum of decaborane itself.

Experimental Section

Materials.—Decaborane was obtained from Callery Chemical Co. and sublimed before use. Reported methods were used to prepare $B_{10}H_8(N_2)_2$,[8] which was purified by sublimation and crystallization.

Mass Spectra.—Spectra were obtained using a Nuclide Corp. 1290 G spectrometer with a heated inlet system. All parts of the instrument except the filament itself were kept below 100° ($B_{10}H_8(N_2)_2$ decomposes at 125°). Intensities for isotope composition determination were determined by adjusting the magnet to put the desired *m/e* on the detector at an accelerating voltage of 4 kV and then scanning over the peak slowly using the accelerating voltage. Intensities were recorded on a strip-chart recorder and corrected for pressure drop with time by repeating the first intensity measurement of each run at the end of the run.

Appearance potential differences were determined from plots of log (ion current) *vs.* apparent voltage, which were parallel for *m/e* 174, 146, and 118.

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Preparation and Some Reactions of Difluoroborane

By T. D. Coyle, J. Cooper, and J. J. Ritter

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Difluoroborane is produced by the direct interaction of boron trifluoride with diborane in the gas phase at 100° or above. Pyrolysis of BF_3–B_2H_6 mixtures at 250° for periods of 30 min to 1 hr, followed by rapid quenching, yields HBF_2–BF_3 mixtures free of B_2H_6. An alternative, synthetically useful route is the reaction of $HB(OCH_3)_2$ with excess BF_3. Difluoroborane undergoes rapid H–F exchange with boron trifluoride and H–D exchange with deuterated diborane but does not exchange boron with diborane. Addition of difluoroborane to propene and isobutene yields *n*-propyldifluoroborane and isobutyldifluoroborane, respectively. Reactions with fluoroethylenes give boron trifluoride, ethylfluoroboranes, and less highly fluorinated olefins.

Introduction

Since our preliminary report of the synthesis of difluoroborane,[1] this compound has been intensively investigated by a variety of physical methods, including nuclear magnetic resonance,[2,3] infrared,[4–8] and microwave[9] spectroscopy. Little information has appeared, however, on the chemistry of this compound, which is the only known fluorohydride of three-coordinate boron. In this paper we report our observations on the preparative reactions utilized in the synthesis of HBF_2 and on aspects of its descriptive chemistry.

Results and Discussion

Preparative Reactions.—Two distinct routes have been found for the preparation of difluoroborane, HBF_2. The first of these is the formation of HBF_2 by the direct interaction of BF_3 and B_2H_6 which occurs, in the absence of catalysts, only under relatively vigorous conditions leading also to pyrolysis of diborane. This is in contrast to the facile hydride–halide exchange reactions observed[10] at room temperature between diborane and boron tribromide or trichloride.[11] The most useful synthetic procedure involves pyrolysis of BF_3–B_2H_6 mixtures at 250° for short periods, under which conditions HBF_2–BF_3 product mixtures containing 30–35% HBF_2 and free of B_2H_6 can be obtained. Calculations based on the thermodynamic data of Porter and Wason[6] show that the pressure of

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(11) The necessary activation can also be provided by subjecting BF_3–B_2H_6 mixtures to an electric discharge.[4] Other potentially useful routes to HBF_2 involve B_2F_4 as a starting material, *e.g.*, the reaction of B_2F_4 with H_2 in a high-frequency discharge[7] or with covalent hydrides in the gas phase: T. D. Coyle and J. J. Ritter, submitted for publication.