discrepancy here is simply too large.

Part of this energy difference could be made up if it was assumed that reaction occurs from the $^4B_2$ state formed directly by absorption prior to internal conversion. If that were the case, one might well expect a wavelength effect. Although we show a small wavelength change of the quantum yields, that change is within experimental error.

It must be pointed out that the substrates are somewhat unstable on ion exchange resins; we could not use HPLC in the analysis, as has been done previously so successfully,[14] because of decomposition. The analysis for free cyanide required brief (30 s) contact with an anion-exchange resin, and this proved satisfactory for the starting materials: *cis*- and *trans*-$Cr(en)_2(CN)_2^+$. As pointed out in the Experimental Section, however, we have evidence for some thermal decomposition of the photochemical product in the solution and on the anion resin. For this reason, the quantum yields for cyanide release, if in error, may be somewhat high.

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**Registry No.** *cis*-$Cr(en)_2(CN)_2^+$, 53302-06-0; *trans*-$Cr(en)_2(CN)_2^+$, 72074-79-4; *cis*-$[Cr(en)_2(CN)_2](ClO_4)$, 56848-41-0; *trans*-$[Cr(en)_2(CN)_2](ClO_4)$, 72074-80-7; *trans*-$[Cr(en)_2Br_2]Br$, 17993-14-5.

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# Intermediates in the Mercury-Photosensitized Reactions of Pentaborane(9)

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We have investigated the Hg-photosensitized reactions of selectively deuterated pentaboranes including 1-$DB_5H_8$ and ($\mu$-D)$B_5H_8$. From the proportions of $H_2$, HD and $D_2$ in the photolysis products we conclude that the primary reactive intermediate leading to decaborane(14) and -(16) is pentaborane(7) resulting from direct loss of molecular hydrogen. The elimination of $H_2$ from any pair of H sites in pentaborane is a random but not strictly statistical process. The existence of the free-radical intermediate $B_5H_8$ is not substantiated. Supportive mechanistic information is obtained from experiments with 1-methyl- and 2-methylpentaboranes.

## Introduction

There is little physical evidence for postulating free-radical intermediates in the mechanisms of boron hydride pyrolyses. However, photochemical studies of $B_5H_9$ have suggested the presence of an intermediate $B_5H_8$ radical to account for the formation of $B_{10}H_{16}$ as one of the isolable reaction products.[1] Burwasser and Pease[2] predicted the photochemical formation of $B_5H_8$ in the 184.9-nm irradiation of pentaborane and deuterium. In the gas-phase radiolysis of pentaborane, Subbanna, Hall, and Koski[3] observed the formation of $(B_5H_8)_2$. They proposed a mechanism in which two $B_5H_8$ radicals couple to form decaborane(16). Grimes and co-workers[4] suggested using a glow discharge to react the postulated pentaboranyl free-radical reaction intermediate with other molecules. Wang et al.[5] investigated the proton-transfer reaction for a series of bases (R) and obtained information on the stability of $B_5H_8$.

$$B_5H_9^+ + R \rightarrow B_5H_8 + RH^+ \qquad (1)$$

The photochemical preparation of $B_{10}H_{16}$ reported by Plotkin and Sneddon[1] was suggested to proceed by a free-radical mechanism.

$$Hg(^1S_0) \xrightarrow[253.7\ \text{nm}]{h\nu} Hg(^3P_1) \qquad (2)$$

$$Hg(^3P_1) + B_5H_9 \rightarrow Hg(^1S_0) + B_5H_8 + H \qquad (3)$$

$$2B_5H_8 \rightarrow B_{10}H_{16} \qquad (4)$$

It is difficult to obtain mechanistic information on these complex reactions solely from product analysis without the use of isotopic labels. Out interest in photochemical intermediates has led to a reexamination of the reaction of $Hg(^3P_1)$ with pentaborane. Our experimental approach is to investigate the photochemical behavior of selectively deuterated pentaboranes and examine the isotopic composition of the reaction products. Photosensitization reactions of 1-methyl- and 2-methylpentaboranes are also investigated.

## Experimental Section

**Instrumentation and Methods.** Infrared spectra were recorded on a Perkin-Elmer Model 337 spectrophotometer using 3-in. gas cells with either sodium chloride or potassium bromide optics. The cells were thoroughly purged with dry nitrogen after cleaning, and background spectra were run before and after employing the cells. Proton NMR spectra were obtained on either a Varian EM-390 or A-60A spectrometer. $^{11}B$ NMR spectra were run on a Bruker HX-90 high-resolution spectrometer in the CW mode. Samples were sealed in vacuo with carbon disulfide solvent. Unless otherwise noted, electron-impact mass spectra were obtained on a Consolidated Electrodynamics Corp. Model 21-103A spectrometer at 70-eV ionizing voltage. Other mass spectra were acquired with an AE1-MS902 instrument. Photoionization mass spectra were obtained with the instrument described by DeStefano and Porter,[6] employing lithium fluoride optics and the 121.6-nm $\alpha$-Lyman emission of hydrogen as the ionizing radiation. Chemical ionization mass spectra in methane were run on the Finnigan Model 3300 gas chromatograph/mass spectrometer employing the gas-inlet system.

Gas chromatograms were obtained on an F and M Corp. Model 810 research gas chromatograph using a flame ionization detector. A 6 ft × $^1/_4$ in. o.d. column operated at 100 °C with 3% OV-101 on 80/100 Chromasorb W-HP support was found to be sufficient for the separation of the decaborane derivatives investigated in this work. Mass spectra (electron impact and chemical ionization) of the decaboranes in carbon disulfide were obtained with the Finnigan Model 3300 gas chromatograph/mass spectrometer with a Systems Industries System 150 data system.

The composition of partially deuterated pentaboranes was resolved from the analysis of the photoionization mass spectra. The absence of fragmentation of the molecular ions produced a spectrum that was a simple summation of the normal isotopic distributions of the parent

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ions (e.g., $B_5H_5D_4^+ + B_5H_6D_3^+ + B_5H_7D_2^+ + B_5H_8D^+$). The reduction of mass spectra (electron impact) of chemical ionization into relative ion compositions [$(P + 1)^+$, $P^+$, $(P - 1)^+$, etc.] was achieved by the successive subtraction of the high-mass normal isotopic distributions from the experimental spectra. Analyses for the relative concentrations of $H_2$, HD, and $D_2$ were determined on the CEC mass spectrometer using calibrations with prepared $H_2/D_2$ mixtures and equilibrated $H_2/HD/D_2$ samples. Intensities were corrected for compositional changes by extrapolation to the initial fillings of the spectrometer's ballast volume.

Unreversed radiation at 253.7 nm was supplied by a Rayonet photochemical reactor, the Southern New England Ultraviolet Co., equipped with 16 R.P.R. 2537-A lamps or replacements, Sylvania G8T5 germicidal lamps. A typical photolysis cell was a 30 mm o.d. × 60 cm cylindrical Vycor vessel. It was joined by a Pyrex to quartz graded seal to a greaseless Teflon valve. After the addition of one or two drops of mercury, the cell was thoroughly evacuated and purged with dry nitrogen (passed through Aquasorb desiccant). The cell was repeatedly "flamed-out" during the purging process. Before use, the cell was irradiated for approximately 1 h in the photochemical reactor and checked for the evolution of any gaseous substances.

**Sample Preparation.** Pentaborane, obtained from the Callery Chemical Co., was repurified by vacuum distillation through U-tube traps. Slow passage of the $B_5H_9$ through a −78 °C trap removed the higher molecular weight impurities. Pure $B_5H_9$ was recovered in a −98 °C trap.

Pentaborane-*d*$_9$ was prepared by the pyrolysis of $B_2D_6$.[7] Final purification of $B_5D_9$ was achieved by slow passage through a −78 °C trap to eliminate a possible $B_5D_{11}$ impurity. No evidence for pentaborane(11) was detected in any of the pyrolysis products.

1-$DB_5H_8$ was prepared by the reaction of DCl with $B_5H_9$ in the presence of $AlCl_3$.[8] The reaction was repeated until no change in the infrared spectrum was observed.

($\mu$-D)$B_5H_8$ was prepared by the method of Gaines and Iorns.[9] By the successive repetition of this procedure with the deuterated products, multiple deuteration of the bridge positions was achieved. Retention of deuterium in the bridge position was noted from infrared spectra which distinguish bridge from terminal B–D stretching frequencies.

1-Methylpentaborane(9) was prepared from pentaborane(9) and methyl bromide under Friedel–Crafts conditions with aluminum chloride catalysts.[10,11] 2-Methylpentaborane(9) was prepared from the quantitive rearrangement of 1-methylpentaborane(9) by employing the base catalyst 2,6-lutidine.[12] The product purities were confirmed by their mass,[13] infrared, and proton NMR spectra.[12,14] The purity of the 1-methylpentaborane(9) was rechecked by photoionization mass spectrometry.[15]

## Results

**Photolyses with Mercury at 253.7 nm. (1) $B_5H_9$.** In a typical photolysis, pentaborane was irradiated at its normal vapor pressure in a 60 cm × 30 mm o.d. Vycor cell equipped with a Teflon valve. A drop of mercury was added to the vessel to ensure saturation. Pentaborane does not absorb radiation directly from the mercury light source at wavelengths transmitted by Vycor.[16] The products of 1-h cumulative irradiation were separated by passing through U-tube traps maintained at −23, −45, and −196 °C. The noncondensable product was hydrogen. Mass and infrared spectra indicated only unreacted pentaborane in the −196 °C trap. A clear, viscous liquid was isolated in the −45 °C trap. Redistillation removed a pentaborane impurity, as noted in the disappearance of the strong peak at *m/e* 64 in the mass spectrum. The 70-eV electron-impact mass spectrum had a high-mass cutoff at *m/e* 126. The photoionization mass spectrum was obtained to confirm the molecular composition. The product recovered in the −23 °C trap was a clear, crystalline solid. A photoionization mass spectrum of this product indicated a molecular ion, $B_{10}H_{14}^+$, and a weak dimer peak, $B_{20}H_{28}^+$, formed by an ion–molecule reaction. The nonvolatile products that remained in the photolysis cell were not analyzed. However, they were observed to effervesce vigorously with the addition of methanol and did not spontaneously enflame when the vessel was vented to the atmosphere. These results agree with those reported by Plotkin and Sneddon.[1] The volatile products of the 253.7-nm mercury photosensitization of pentaborane are hydrogen, a decaborane(16),[17] and decaborane(14).

**Table I.** Hydrogen Product Compositions of Photolyses of Equimolar $B_5H_9/B_5D_9$ Mixtures with Hg at 253.7 nm

| time irradiated, s | mol fractions obsd | | | calcd[c] equil compn | | | $K_{obsd}/K_{eq}$[a,b] |
|---|---|---|---|---|---|---|---|
| | $H_2$ | HD | $D_2$ | $H_2$ | HD | $D_2$ | |
| | | | A. Quartz Photolysis Cell | | | | |
| 200 | 0.23 | 0.19 | 0.58 | 0.08 | 0.37 | 0.55 | 0.08 |
| 50 | 0.38 | 0.26 | 0.37 | 0.27 | 0.48 | 0.25 | 0.14 |
| 600 | 0.45 | 0.31 | 0.24 | 0.44 | 0.43 | 0.13 | 0.27 |
| 650 | 0.48 | 0.30 | 0.22 | 0.48 | 0.41 | 0.11 | 0.26 |
| | | | B. Vycor Photolysis Cell | | | | |
| 10 | 0.10 | 0.10 | 0.80 | 0.01 | 0.16 | 0.83 | 0.03 |
| 10 | 0.15 | 0.13 | 0.72 | 0.03 | 0.25 | 0.73 | 0.05 |
| 10 | 0.18 | 0.15 | 0.67 | 0.04 | 0.29 | 0.67 | 0.06 |
| 10 | 0.22 | 0.18 | 0.60 | 0.07 | 0.36 | 0.58 | 0.07 |
| 10 | 0.18 | 0.23 | 0.59 | 0.06 | 0.34 | 0.61 | 0.15 |
| 20 | 0.32 | 0.20 | 0.48 | 0.16 | 0.45 | 0.39 | 0.08 |
| 20 | 0.33 | 0.25 | 0.43 | 0.20 | 0.47 | 0.34 | 0.13 |
| 20 | 0.36 | 0.25 | 0.40 | 0.23 | 0.47 | 0.29 | 0.13 |

[a] $K_{obsd} = (HD)^2/(H_2)(D_2)$ (experimental). [b] $K_{eq} = 3.28$ (25 °C): D. Rittenberg, W. Bleakney, and H. C. Urey, *J. Chem. Phys.*, **2**, 48 (1934). [c] The equilibrium compositions were calculated from the relative abundances of H and D in the product.

**(2) $B_5H_9/B_5D_9$.** An equimolar mixture of pentaborane and deuterated pentaborane (total pressure 5 torr) was added to a greaseless quartz photolysis cell (28 mm o.d. × 40 cm). A small mercury pool and a Teflon-clad stir bar were placed at the bottom of the cylindrical cell. Several successive photolyses were carried out at 253.7 nm in a Rayonet photochemical reactor, with the removal of the hydrogen product between the individual runs. The relative yields of $H_2$, HD, and $D_2$, as determined by mass spectrometry, are summarized in Table I. An independent equimolar preparation of pentaborane and deuterated pentaborane (total pressure 28 torr) was transferred to a greaseless Vycor cell (30 mm o.d. × 60 cm). A drop of liquid mercury was added to ensure saturation. The results of several successive photolyses in the photochemical reactor are summarized in Table I.

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(15) Small amounts of 1,2-dimethylpentaborane(9) were detected at higher source pressures (ca. 50 $\mu$m). The pressure dependence of the relative intensities observed at high-mass cutoffs 78 and 92 indicate that charge transfer occurs from 1-methylpentaborane to 1,2-dimethylpentaborane. Further vacuum distillation through U-tube traps reduced the disubstituted fraction from NMR and mass spectral detection. The production of the dimethyl impurity may be inherent under the thermal conditions (100 °C) of the Friedel–Crafts alkylation; i.e., some thermal rearrangement of the 1-methylpentaborane occurs, followed by a successive alkylation of the apical boron atom to produce 1,2-dimethylpentaborane.

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(17) An alternate structure is possible for the decaborane(16) reported in the literature as 2,2′-$B_{10}H_{16}$. A discussion of the decaboranes(16) and the results of extended Hückel calculations for bridge–terminal linked pentaboranyl units is presented by G. A. Kline, Ph.D. Thesis, Cornell University, 1978.

**Table II.** Isotope Composition of Hydrogen Gas Produced by Hg Photosensitization of Selectively Deuterated Pentaboranes

| | | atom % D | | mol fraction H product obsd | | | | | $(H_2/HD)_{calcd}$ | |
|---|---|---|---|---|---|---|---|---|---|---|
| compd | irradn time, s | compd | H product | $H_2$ | HD | $D_2$ | $K_{obsd}$[c] | $(H_2/HD)_{obsd}$ | nonstatistical | statistical |
| 1-$DB_5H_8$ | 20 | 11.1[a,b] | 12.8 | 0.751 | 0.243 | 0.007 | 11.2 | 3.09 | 3.0 | 3.5 |
| ($\mu$-D)$B_5H_8$ | 20 | 10.6[a] | 8.5 | 0.821 | 0.174 | 0.005 | 7.4 | 4.72 | 7.0 | 3.5 |
| 65% bridge-deuterated pentaboranes | 20 | 28.9[d] | 21.2[d] | 0.662 | 0.333 | 0.045 | 3.7 | 2.0 | 2.1 | 1.1 |

[a] Composition determined from relative intensities of *m/e* 65 and 64 in 70-V electron impact mass spectrum. [b] Composition determined from alcoholysis in methanol. [c] $K_{obsd} = (HD)^2/(H_2)(D_2)$; $K_{eq} = 3.28$ (25 °C); see Table I. [d] Composition determined from photoionization mass spectrum at 121.6 nm.

**(3) 1-$DB_5H_9$.** A sample of 1-$DB_5H_8$ ($P$ = 20 torr) and Hg was irradiated at 253.7 nm for 20 s in a greaseless Vycor cell (30 mm o.d. × 50 cm). Mass spectral analysis of the hydrogen product is shown in Table II.

**(4) ($\mu$-D)$B_5H_8$.** A sample of ($\mu$-D)$B_5H_8$ ($P$ = 20 torr) and Hg was irradiated for 20 s at 253.7 nm in a Vycor cell (30 mm o.d. × 50 cm). A mixture of bridge-deuterated pentaboranes was irradiated at 253.7 nm with mercury for 20 s in a greaseless Vycor cell (30 mm o.d. × 50 cm). The hydrogen product analyses from these experiments are given in Table II.

**(5) $B_5H_9$ in the Presence of $H_2/D_2$.** Pentaborane and mercury were irradiated at 253.7 nm in the presence of $H_2$, $D_2$, and equilibrium mixtures of $H_2/HD/D_2$. The addition of hydrogen (deuterium) in the photolysis of mercury and pentaborane was observed not to affect measurably the quantity of pentaborane that reacted. The irradiation of Hg and $B_5H_9$ ($P$ = 50 torr) for 1 h in a quartz cell (28 mm o.d. × 40 cm) produced approximately a 20% decrease in the pentaborane both in the presence of $D_2$ ($P$ = 220 torr) and in the absence of added $D_2$. The mass and infrared spectra of the pentaborane recovered from the photolysis with $D_2$ showed the presence of $B_5H_8D$. A sample of $B_5H_9$ ($P$ = 26 torr) and $D_2$ ($P$ = 0.5 torr) was irradiated with Hg in a Vycor cell (30 mm o.d. × 60 cm) for 100 s. The hydrogen product analysis revealed a composition of $H_2/HD/D_2$ = 0.46/0.03/0.51, compared to the starting material composition <0.001/0.003/0.993. A sample containing $B_5H_9$ ($P$ = 30 torr) and 29 torr of an equilibrium hydrogen mixture was irrdiated successively for 20, 10, and 50 s in a quartz cell (28 mm o.d. × 40 cm) in the presence of Hg. A mass spectrometric analysis of the hydrogen composition was obtained after each irradiation by sampling of the reaction mixture. Analysis of the pentaborane after 50-s irradiation showed that little $B_5H_8D$ had been formed. The hydrogen product analyses are summarized in Table III.

**(6) Methylpentaboranes.** 1-Methylpentaborane was irradiated at its normal vapor pressure in a greaseless Vycor cell (30 mm o.d. × 60 cm) in the presence of mercury vapor. Following each hour of cumulative irradiation, the volatile material was fractionally distilled through U-tube traps and the condensable compounds that passed through the −45 °C trap were returned for further irradiation. For 1000 s of irradiation, the yield of $H_2$ was determined to be approximately 1 mmol by observation of the pressure changes. The composition of the noncondensable $H_2$ gas was confirmed by mass spectrometry. The condensable products of 3-h irradiation were combined, fractionally distilled through U-tube traps maintained at −6, −45, and −196 °C, and analyzed. No significant fraction was obtained in the −45 °C trap. Unreacted 1-methylpentaborane was recovered in the −196 °C trap. Chemical ionization analysis of the products trapped at −6 °C indicated little ion fragmentation, with formation of a $(P - H)^+$ ion at *m/e* 151 as the only major feature.

**Table III.** Hydrogen Product Analyses of the 253.7-nm Photolysis of $B_5H_9$ and Hg and an Equilibrium Mixture of Hydrogen/Deuterium

| | mol fraction in product[a] | | | |
|---|---|---|---|---|
| irradn time, s | $H_2$ | HD | $D_2$ | $K_{obsd}$[b] |
| 0 | <0.001 | 0.022 | 0.978 | 3.28 ($K_{eq}$) |
| 20 | 0.010 | 0.025 | 0.965 | 0.006 |
| 10 | 0.008 | 0.028 | 0.964 | 0.10 |
| 50 | 0.012 | 0.030 | 0.958 | 0.08 |

[a] The $H_2$ fraction was corrected for the calibrated relative abundance of $D_2^+/D^+$ in the mass spectrum. [b] $K_{obsd} = (HD)^2/(H_2)(D_2)$.

2-Methylpentaborane was irradiated at its vapor pressure in a greaseless Vycor cell in the presence of mercury vapor. The products of 1-h cumulative irradiation were passed through U-tube traps maintained at −64.5 and −196 °C. Unreacted starting material was recovered from the −196 °C trap. The gas chromatographic analysis of the products collected at −63.5 °C showed four major peaks. The electron-impact mass spectrum corresponding to one chromatogram peak displayed a high-mass cutoff at *m/e* 152. The corresponding mass spectrum obtained by chemical ionization in methane displayed *m/e* 151 as the dominant $^{11}B_{10}^+$ species. The electron-impact mass spectrum corresponding to a second chromatogram peak had a high-mass cutoff at *m/e* 154. The chemical ionization mass spectrum in methane showed a high-mass cutoff at *m/e* 155 with very little contribution at higher masses. The other two gas chromatogram peaks both had high-mass cutoffs at *m/e* 152 in their corresponding electron-impact mass spectra. Their chemical ionization mass spectra were similar with the only major contribution having a high-mass cutoff at *m/e* 151.

The proton NMR spectrum of the prodcucts in the −6 °C trap from the photolysis of 1-$CH_3B_5H_8$ was obtained in carbon disulfide. Three methyl proton resonances were observed. A resonance observed at $\delta_{Me_4Si} = 0.11 \pm 0.02$ coincided with the methyl proton resonance of 1-$CH_3B_5H_8$. The third resonance was observed at $\delta_{Me_4Si} = 0.79 \pm 0.02$.

The proton NMR spectrum of the products in the −63.5 °C trap from the photolysis of 2-$CH_3B_5H_8$ was obtained in carbon disulfide. Two methyl proton resonances were observed. A resonance coincided with a peak in the products of 1-$CH_3B_5H_8$ above ($\delta_{Me_4Si} = 0.79 \pm 0.02$). A resonance was observed at $\delta_{Me_4Si} = 0.47 \pm 0.02$, corresponding to the methyl proton resonance in 2-$CH_3B_5H_8$.

## Discussion

The results in the photolyses of equimolar mixtures of $B_5H_9$ and $B_5D_9$ contain significant deviations from isotopic equilibrium in the hydrogen products. In each of the experimental runs, the fraction of HD observed was lower than expected in an equilibrium composition calculated from the relative abundances of H and D in the hydrogen product. The elimination of molecular hydrogen from pentaborane is necessary to account for this hydrogen composition. The argument for molecular elimination of hydrogen is strengthened when the reactions of the free hydrogen atoms are considered. One influence of free hydrogen atoms in a $B_5H_9/B_5D_9$ system would be to equilibrate the hydrogen fraction through the exchange reactions

$$H + B_5D_9 \rightarrow B_5D_8H + D \qquad (5)$$

$$D + B_5H_9 \rightarrow B_5H_8D + H \qquad (6)$$

Boranes are known to react with hydrogen atoms by homolytic substitution.

$$D + BH \xrightarrow[S_H2]{} BD + H \qquad (7)$$

In the photolyses of $B_5H_9$ and Hg with $D_2$, $B_5H_8D$ is observed in the products. The mechanism

$$Hg(^3P_1) + D_2 \rightarrow Hg(^1S_0) + 2D \qquad (8)$$

$$D + B_5H_9 \rightarrow B_5H_8D + H \qquad (9)$$

is suggested. A more significant factor in the equilibration of the hydrogen products is a metathetical chain reaction.[18,19]

$$H + D_2 \rightleftarrows HD + D \qquad (10)$$

$$D + H_2 \rightleftarrows HD + H \qquad (11)$$

The formation of H (D) atoms rapidly equilibrates a hydrogen–deuterium mixture. Reactions 10 and 11 may account for much of the HD that is observed in the photolysis products of $B_5H_9/B_5D_9/Hg$ (Table I). A source of H (D) atoms is reaction 8. The results obtained (Table III) from the photolysis of Hg and $B_5H_9$ in an equilibrium hydrogen–deuterium mixture show a large relative increase in the fraction of $H_2$. This distinct perturbation from equilibrium supports the proposal for molecular hydrogen elimination in the $Hg(^3P_1)$ photosensitization of $B_5H_9$. If H atoms are eliminated (reaction 3), strong evidence of reaction 10 would be expected.

The results of the photolyses of the selectively deuterated pentaboranes (Table III) indicate elimination of hydrogen with deviations from equilibrium in the hydrogen products of $1\text{-}DB_5H_8$ and $(\mu\text{-}D)B_5H_8$.

It is evident from the data in Table II that most pairs of H atoms in the pentaborane molecule may participate in $H_2$ elimination reactions. However, it is also evident that the process is not purely statistical. The quantity of $D_2$ due to elimination of two D atoms in bridge sites of partially deuterated pentaboranes is less than expected on a strict statistical basis. We have estimated the proportions of $H_2$ and HD expected for each deuterated pentaborane if we assume (1) a nonstatistical distribution requiring that only H atoms along an edge of a pentaborane polyhedron or adjacent terminal–bridge hydrogen atoms are eliminated (a total of 16 H–H pairs) and (2) a statistical distribution assuming any pair of H atoms may be eliminated (a total of 36 H–H pairs). The results shown in Table II favor a nonstatistical distribution if secondary isotope effects are neglected. Regardless of the importance of secondary isotope effects, the results indicate a high degree of site randomness for hydrogen elimination. The detection of $^{11}B_{10}H_{14}D_2^+$ (*m*/*e* 128) in the mass spectrum of the photolysis products of $1\text{-}DB_5H_8$ suggests that the apical hydrogen atom is not compulsory for the reaction

$$Hg(^3P_1) + 2B_5H_9 \rightarrow B_{10}H_{16} + H_2 \qquad (12)$$

It is also noted that $1\text{-}CH_3B_5H_8$ without an apical hydrogen reacted with $Hg(^3P_1)$ to form $B_{10}H_{14}(CH_3)_2$.

The NMR analyses of irradiated samples of methylpentaborane show no evidence of isomerization of either the 1- or the 2-methyl isomer. These observations suggest the general conclusion that the transfer of a quantum of energy from a triplet mercury atom to form an electronically excited state of pentaborane is not the dominant process in the photochemistry observed in these experiments. It is observed that the reactions

$$1\text{-}CH_3B_5H_8 \xrightarrow[\Delta]{} 2\text{-}CH_3B_5H_8 \qquad (13)^{10}$$

$$1\text{-}CH_3B_5H_8 \xrightarrow[\text{base}]{} 2\text{-}CH_3B_5H_8 \qquad (14)^{12}$$

occur quantitatively. If the reaction

$$^3Hg + 1\text{-}CH_3B_5H_8 \rightarrow {}^1Hg + {}^3(1\text{-}CH_3B_5H_8) \qquad (15)$$

is occurring in our experiments, then some evidence of the reactions

$$^3(1\text{-}CH_3B_5H_8) \rightarrow 1\text{-}CH_3B_5H_8{}^v \quad \text{(intersystem crossing)} \qquad (16)$$

$$1\text{-}CH_3B_5H_8{}^v \rightarrow 2\text{-}CH_3B_5H_8 \quad \text{(isomerization)} \qquad (17)$$

$$^3(1\text{-}CH_3B_5H_8) \rightarrow {}^3(2\text{-}CH_3B_5H_8) \quad \text{(isomerization)} \qquad (18)$$

$$^3(2\text{-}CH_3B_5H_8) \rightarrow 2\text{-}CH_3B_5H_8 \quad \text{(intersystem crossing)} \qquad (19)$$

would be expected. Consequently, it is suggested that the interaction of a pentaborane with a triplet mercury atom involves the irreversible formation of an intermediate that reacts to form higher molecular weight products and molecular hydrogen. Decaborane(14) and decaborane(16) are the major products in the 253.7-nm photolysis of pentaborane(9) and mercury.[1] The mass spectral analysis of the photolysis products of the methylpentaboranes indicate the formation of dimethyldecaborane(14) and dimethyldecaborane(16) with respective high-mass cutoffs at *m*/*e* 152 and 154.

The proton NMR spectra of the 1-methylpentaborane photolysis products reveal significant retention of the apical methyl proton resonance. This is probably embodied in the dimethyldecaborane(16) fraction of the sample. The appearance of some basal methyl proton resonance suggests some isomerization in a pentaboranyl fragment. The isomerization probably occurs during the formation of the reactive intermediate or of the product molecule. No isomerization is indicated in the proton NMR spectra of the products of 2-methylpentaborane. Equations 13 and 14 argue persuasively that 2-methylpentaborane is the more stable isomer of pentaborane. Consequently, some thermodynamically favored rearrangement of a pentaboranyl fragment is occurring during the formation of dimethyldecaborane(16).

The resonance at $\delta_{Me_4Si} = 0.79$ is observed in the proton NMR spectra of the products of either isomer of methylpentaborane. This resonance is tentatively assigned to the methyl protons in dimethyldecaborane(14). On the basis of the collective evidence obtained in this study, we propose that the primary step in the reaction of $Hg(^3P_1)$ with $B_5H_9$ leads to the formation of a reactive intermediate $(B_5H_7)^*$ through the process

$$Hg(^3P_1) + B_5H_9 \rightarrow Hg(^1S_0) + (B_5H_7)^* + H_2 \qquad (20)$$

Stable reaction products may be accounted for by the mechanism

$$(B_5H_7)^* + B_5H_9 \rightarrow B_{10}H_{16}^* \begin{array}{l} \rightarrow B_{10}H_{14} + H_2 \\ \rightarrow B_{10}H_{16} \end{array} \qquad (21)$$

Possibly, the most attractive feature of this mechanism is that the formation of the products requires only a collision of a reactive intermediate, $(B_5H_7)^*$, with a thermal pentaborane molecule. In the free-radical mechanism, two $B_5H_8$ intermediates must react to form $B_{10}H_{16}$. For this radical dimerization to occur, $B_5H_8$ must be relatively long-lived, i.e., stable in the reaction system.

In summary, it is proposed that the 253.7-nm mercury photosensitization of pentaborane(9) involves the elimination

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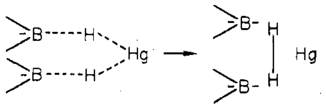
[18] S. W. Benson, "Thermochemical Kinetics", 2nd ed., Wiley-Interscience, New York, 1976, p 220.

[19] A. F. Trotman-Dickenson, *Adv. Free-Radical Chem.*, **1**, 1 (1965).

of molecular hydrogen. The nonbridge hydrogens appear to be favored in the nonstatistical distribution of the product. This supports the arguments that the hydrogen molecule is formed in a concerted reaction with $Hg(^3P_1)$. The coordination of the $Hg(^3P_1)$ atom to a pair of hydrogen atoms in pentaborane results in the formation of the hydrogen molecule. Structures I and II in reaction 22 are a schematic representation of the interaction. A similar interpretation is reported for the $Hg(^3P_1)$ photosensitization of propane.[20] The side-on orientation of Hg to $H_2$ is consistent with Callear's[21] study of the reaction of $Hg(^3P_{1,0})$ with hydrogen.



I II (22)

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**Registry No.** $B_5H_9$, 19624-22-7; $B_5D_9$, 24034-84-2; 1-$DB_5H_8$, 63643-91-4; ($\mu$-D)$B_5H_8$, 16743-79-6; 1-methylpentaborane, 19495-55-7; 2-methylpentaborane, 23753-74-4.

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# Boron Halide Clusters and Radicals: Synthesis and Interconversions of the Three Oxidation States of a Nine-Boron Polyhedron

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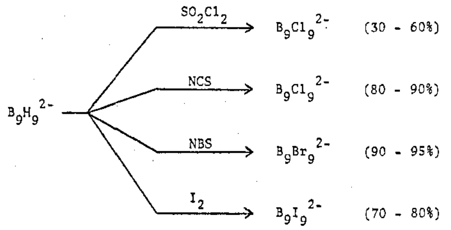
The facile synthesis of the perhalogenated nonahydrononaborates $B_9X_9^{2-}$ (X = Cl, Br, I) under aprotic conditions from $B_9H_9^{2-}$ is described. Oxidations of the perchloro and perbromo anions have yielded the corresponding neutral clusters $B_9Cl_9$ and $B_9Br_9$. Novel borane radicals of the type $B_9X_9^{-}\cdot$ (X = Cl, Br, I) have been isolated as air-stable, colored salts via chemical oxidation of $B_9X_9^{2-}$ or reduction of $B_9X_9$. The redox sequence $B_9X_9^{2-} \rightleftharpoons B_9X_9^{-}\cdot \rightleftharpoons B_9X_9$ has been established. It is likely that all three oxidation states retain the basic tricapped trigonal-prismatic ($D_{3h}$) geometry characteristic of the parent $B_9H_9^{2-}$ structure. This behavior is unusual for nonmetallic polyhedra, and extensive involvement of the halogen substituents in cage bonding is suggested.

## Introduction

The family of polyhedral boranes $B_nH_n^{2-}$ ($6 \leq n \leq 12$) have exceptional stability as predicted by theoretical MO calculations and empirical electron-counting rules.[2,3] These species have closed-shell electron configurations with the requisite ($2n + 2$) skeletal electrons. Formally, the ($2n + 1$) family of $B_nH_n^{-}\cdot$ radicals and $2n$ neutral $B_nH_n$ species can be generated by one- and two-electron oxidations, respectively. Indeed an EPR spectrum from the probable $B_{10}H_{10}^{-}\cdot$ radical has been observed in the electrolytic oxidation of $B_{10}H_{10}^{2-}$.[4] A well-resolved, complex EPR spectrum obtained during the air oxidation of $B_9H_9^{2-}$ in ethereal solvents has been used to support the existence of $B_8H_8^{-}\cdot$ as one of the transient products.[5] Nevertheless, neither of these unstable anions was isolable. The hypothetical $B_nH_n$ neutral boranes should be extremely unstable and none has been observed to date.

Scheme I



In sharp contrast, the perhalogenated derivatives of these boranes are well established in both the dianionic and neutral oxidation states. For example, $B_{10}Cl_{10}^{2-}$, $B_{10}Br_{10}^{2-}$, $B_{12}Cl_{12}^{2-}$, and $B_{12}Br_{12}^{2-}$ are known as are the neutral clusters $B_4Cl_4$, $B_8Cl_8$, $B_9Cl_9$, $B_9Br_9$, and $B_9Cl_8H$.[6,7] Massey's investigations have definitively established the existence and geometry of the neutral nine-boron halide clusters $B_9Cl_9$ and $B_9Br_9$.[7b,7d] The stability of these clusters in spite of their being formally two-electron deficient ($2n$ skeletal electrons) has been postu-

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