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The Course of Base-catalyzed Hydrogen Exchange in Decaborane[1]

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Generation of an anion of decaborane in a variety of deuterio acid-base media has shown that isotopic hydrogen exchange first occurs at the bridge positions. This result allows the conclusion that the bridge hydrogens are acidic hydrogen atoms attached to decaborane. Continued exchange or equilibration of decaborane (bridge-d_4) in basic solvents affords decaborane which is labelled in terminal positions. A mechanistic rationale is presented.

An earlier communication from this Laboratory[2] briefly stated the conclusions derived from exchange studies of deuterium oxide and chloride with decaborane. That work is amplified in the present paper.

The acidic nature of decaborane was first described by Guter and Schaeffer[3] who demonstrated its monoprotic character with bases and indicated two possible paths for the production of hydrogen ion in aqueous media. Path 1 involves the simple

$$B_{10}H_{14} + H_2O \rightleftharpoons B_{10}H_{13}^- + H_3O^+ \qquad (1)$$

$$B_{10}H_{14} + H_2O \rightleftharpoons B_{10}H_{14}^-OH_2^+ \qquad (2a)$$

$$B_{10}^-H_{14}^+OH_2 + H_2O \rightleftharpoons B_{10}H_{14}^-OH + H_3O^+ \qquad (2b)$$

ionization of decaborane to produce the $B_{10}H_{13}$ anion. Paths 2a and 2b involve the reaction of ionization of the resulting ion-dipole. According to Guter and Schaeffer[3] both paths are observed. Dissolution of decaborane in aqueous media results in the rapid production of hydrogen ion followed by the slow production of additional hydrogen ion. The rate of the slower process is not dependent upon hydrogen ion concentration[3] and this slower process probably involves the rate-determining step 2a and the formation of a strong acid, the ion-dipole. The process 2 must be reversible but it is logical to assume that the hydrolysis of decaborane proceeds through the ion-dipole intermediate.[4]

$$B_{10}H_{14} + 2H_2O \rightleftharpoons B_{10}H_{14}^-OH + H_3O^+ \longrightarrow H_2 + B_{10}H_{13}OH + H_2O$$

The existence of path 1 has been further illustrated by the isolation of stable salts which contain the $B_{10}H_{13}$ anion.[5]

The question of the structural character of the acidic hydrogen removed from decaborane by path 1 immediately arises. In principle, a determination of whether the hydrogens were bonded to boron in bridge or terminal positions appeared possible by a study of the exchange of decaborane with deuterio systems containing Brönsted acids and bases. Such exchanges were carried out under a variety of conditions and the positions of the deuterium labels were determined by infrared spectral analysis.

Infrared Spectra of $B_{10}H_{14}$ and $B_{10}D_{14}$.—The assignment of the characteristic terminal and bridge B–H and B–D infrared absorption bands was accomplished by the study of decaborane and perdeuterodecaborane in carbon disulfide solutions. Perdeuteriodecaborane was prepared by the pyrolysis of perdeuteriodiborane in a static system at 100°.

Figures 1 and 2 are the infrared spectra of decaborane and perdeuteriodecaborane, respectively. The very strong absorption at 2565 cm.$^{-1}$ in the spectrum of decaborane has been assigned to the B–H terminal stretching frequency by a number of authors.[6,7] Deuteration lowers this frequency by a factor of 1.33 to 1925 cm.$^{-1}$. The reported frequency ratio for normal and deuterated alkyl diboranes is 1.34.[7] Absorption bands due to the bridge hydrogens are more complex. According to Hrostowski and Pimentel[6] the bridge hydrogen stretching frequency region is 1800–2140 cm.$^{-1}$. Shapiro, *et al.*,[7] point out that the so called "characteristic" bridge absorption is quite dependent on the identity of the parent boron hydride. They have accordingly assigned absorptions in the 1500–1610 cm.$^{-1}$ region to the B–H bridge stretching frequencies of a series of alkyl diboranes. Bands in the 1600–2220 cm.$^{-1}$ region are ascribed to the B–H bridge by Bellamy, *et al.*[8] The spectrum of decaborane vapor determined in this Laboratory contains a strong absorption at 1510 cm.$^{-1}$ not apparent in carbon disulfide solution because of cut-off by carbon disulfide, but no other bands are exhibited up to 1885 cm.$^{-1}$. Two sharp, but not intense, bands appear at 1885 and 1925 cm.$^{-1}$. These bands are considered to be due to bridge hydrogen stretching by the present authors. Deuteration of the bridge positions in decaborane should place the frequency of the B–D bridge absorption near 1885 cm.$^{-1}/\sqrt{2}$ or near 1400 cm.$^{-1}$. Perdeuteriodecaborane does indeed have a sharp, low intensity band, not present in decaborane, at 1390 cm.$^{-1}$. The deuteration of the decaborane bridges thus produces a stretching frequency ratio of 1.36.

Exchange with Dioxane–Deuterium Oxide.—Table I summarizes the results obtained in the exchange of decaborane with deuterium oxide in dioxane solution at room temperature. Two proper-

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[1] This research was carried out under Army Ordnance Contract DA-01-021 ORD 5135.

[2] M. F. Hawthorne and John J. Miller, THIS JOURNAL, **80**, 754 (1958).

[3] G. A. Guter and G. A. Schaeffer, *ibid.*, **78**, 3456 (1956); Abstracts of Papers, 131st Meeting Am. Chem. Soc., Miami, Florida, p. 3R, 1957.

[4] The kinetic results of R. W. Atterbury, *J. Phys. Chem.*, **62**, 1457 (1958), while difficult to evaluate due to the complexity of the reaction sequence, clearly indicate the production of a relatively stable intermediate.

[5] Unpublished work, M. F. Hawthorne, A. R. Pitochelli, R. D. Strahm and J. J. Miller. Also M. F. Hawthorne, THIS JOURNAL, **80**, 3480 (1958). The $B_{10}H_{13}$ anion absorbs at 268 mμ, ε 2450 and 335 mμ, ε 1770 in a variety of solvents and in the presence of several cations.

[6] H. J. Hrostowski and G. C. Pimentel, *ibid.*, **76**, 998 (1954).

[7] I. Shapiro, C. O. Wilson and W. J. Lehmann, *J. Chem. Phys.*, **29**, 237 (1958).

[8] L. J. Bellamy, W. Gerrard, M. F. Lappert and R. L. Williams, *J. Chem. Soc.*, 2412 (1958).

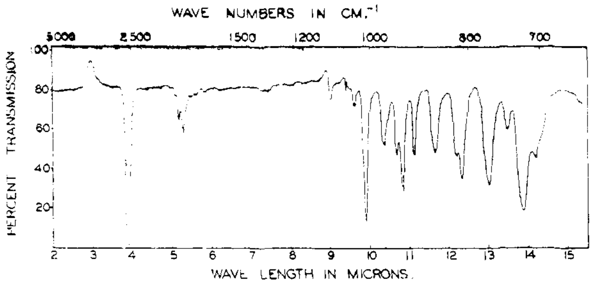

Fig. 1.—Decaborane.

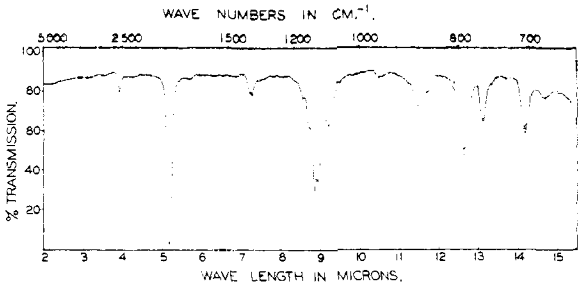

Fig. 2.—Perdeuteriodecaborane.

ties of exchanged decaborane samples were monitored; deuterium content and the characteristics of the observed B–D stretching bands. The experimental portion describes the analytical techniques employed. These results clearly demonstrate the initial entrance of deuterium to bridge positions followed by slower entrance to terminal positions. In no case have more than eight deuterium atoms been found in the product. After 72 hours of equilibration, hydrolysis of the decaborane placed in the reaction mixture is appreciable and no reactions of longer duration were employed. Higher initial concentrations of deuterium oxide and/or longer reaction times would probably introduce more deuterium.

TABLE I

RESULTS OF D_2O–$B_{10}H_{14}$ EXCHANGE EXPERIMENTS IN DIOXANE SOLUTION AT ROOM TEMPERATURE

Sample no.	Equilibration time, hr.	Initial concn., mole/l. $B_{10}H_{14}$	D_2O	B–D infrared absorption	Deuterium/mole
1	0.15	0.083	3.10	Bridge + extremely weak terminal	2.3
2	0.15	.167	6.20	Bridge + very weak terminal	4.6
3	2.00	.167	6.20	Bridge + weak terminal	5.2
4	36.0	.083	3.10	Bridge + moderate terminal	6.2
5	72.0	.120	1.55	Bridge + strong terminal	7.5

Exchange by Neutralization of Sodium Decaborane with Deuterium Chloride—The reaction of boron hydrides with sodium hydride was first described by Hough and Edwards.[9] Decaborane reacts with sodium hydride in ether to produce one mole of hydrogen per mole of decaborane, and a yellow solution of sodium decaborane. Neutralization with hydrogen chloride gas provides sodium chloride and decaborane in 90–98% yield. Removal of the solvent from ethereal sodium decaborane gives a yellow solid which retains ether tenaciously. The color is reduced as ether is removed under high vacuum. Ultraviolet spectra ethereal solutions of this material are characteristic of the $B_{10}H_{13}$ anion.[5]

Treatment of sodium decaborane, prepared as described above, with deuterium chloride gave a sample of decaborane containing 0.9 deuterium atoms per mole. Examination of the infrared spectrum of this material showed a small absorption in the B–D bridge region and a decrease in the B–H bridge absorption from that of decaborane. Thus the deuterium enters the bridge position. A sample of this exchanged material was treated with sodium hydride and then again neutralized with deuterium chloride. This stepwise formation of the anion and addition of deuterium chloride was repeated six times. Table II briefly summarizes the results.

TABLE II

$NaB_{10}H_{13}$–DCl REACTIONS

No. of stepwise reactions	Infrared spectra relation to $B_{10}H_{14}$ B–H	B–D	Deuterium/mole
1	Bridge slightly decreased	Bridge slightly increased	0.9
4	Bridge decreased	Bridge increased	3.4
6	Terminal not apparently affected	Unable to determine[10]	4.7

The Role of Solvent in the Exchange with Deuterium Chloride and the Deuterium Migration from Bridge to Terminal.—The exchange of decaborane with deuterium chloride in the presence of solvent was carried out at room temperature. Table III summarizes the results obtained with dioxane and methylene chloride solvents. It is to be noted that exchange occurred only in the presence of the basic solvent, dioxane.

TABLE III

EXCHANGE OF $B_{10}H_{14}$ WITH DCl AT ROOM TEMPERATURE

Solvent	Exchange time, hr.	Initial quantities, moles DCl	$B_{10}H_{14}$	B–D infrared absorption	Deuterium/mole
Dioxane	114	0.036	0.0024	Bridge + strong	6.2
Dioxane	96	.032	.0016	terminal	5.9
Methylene chloride	93	.038	.0024	Identical with $B_{10}H_{14}$	0

Equilibration of a sample of decaborane, which contained essentially only bridge deuterium and analyzed for 4.7 deuterium atoms per molecule, in dioxane for one hour at room temperature gave

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[9] W. V. Hough and L. J. Edwards, Abstracts of Papers, 133rd Meeting Am. Chem. Soc., San Francisco, Calif., 1958, p. 28-L.

[10] Unfortunately the B–D terminal band at 1925 cm.⁻¹ cannot be followed at low B–D terminal concentration because of a B–H bridge band at the same frequency. It is apparent that little B–D terminal is present, however. After six exchanges a slight increase in the 1925 cm.⁻¹ band is detectable.

a sample which exhibited an absorption band in its infrared spectrum due to terminal B–D stretching. This band is much more intense than it was prior to the equilibration. This is taken as proof that deuterium has moved from bridge positions to terminal positions. That a basic solvent is necessary for this rearrangement was illustrated by equilibration of an identical decaborane sample in methylene chloride solution. No migration of deuterium was observed.

Shapiro, Lustig and Williams[11] recently have reported a nuclear magnetic resonance study of the dioxane–deuterium oxide exchange and dioxane catalyzed deuterium migration reactions. Their results show that deuterium first enters the bridge positions and will migrate to terminal positions (5, 7, 8 and 10) neighboring the bridge positions. Their results further extend and substantiate our conclusions.

Possible Exchange Mechanism.—The very rapid exchange of bridge hydrogen with deuterium oxide suggests that this reaction is related to the rapid ionization of decaborane shown in (1) above. This is further illustrated by the series of experiments in which the sodium salt of decaborane was repeatedly formed and neutralized with deuterium chloride. It therefore appears most likely that the $B_{10}H_{13}$ anion is formed by the removal of a proton from a bridge position and that deuterium may be introduced when the reverse process occurs.

The Lewis base-catalyzed migration of bridge deuterium to the 5, 7, 8 and 10 terminal hydrogen positions most likely occurs as described by Shapiro, Lustig and Williams.[11] The attack of base upon the 6 or 9 borons which is required by this mechanism is exemplified by the recent finding of Lipscomb and Reddy[12] that acetonitrile attacks these positions to form a substitution compound.

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Experimental

Materials.—Decaborane was obtained from the American Potash and Chemical Corporation and was resublimed before use. Dioxane was purified according to the method described by Fieser[13] and deuterium chloride was prepared by the method of Brown.[14]

Instrumental Methods.—The infrared spectra were obtained on a Perkin-Elmer model 21 spectrophotometer with sodium chloride optics. All spectra, with the exception of Fig. 2 and that of decaborane vapor were obtained using 15.5–15.6 mg. of sample in one milliliter of carbon disulfide in a 0.5 mm. cell. The spectrum exhibited in Fig. 2 was the same; however, only 11.2 mg. of sample was used.

Mass spectrometric measurements were made on a Consolidated Engineering Corporation type 21-620 instrument.

Dioxane Deuteration.—Decaborane samples were dissolved in dioxane and deuterium oxide was added. The heterogeneous mixtures were stirred for the desired length of time and were then flash evaporated under high vacuum (10^{-5} mm.) at 25°. The residues were extracted with ether to remove deuterated decaborane from the deuterioboric acid produced by hydrolysis. Evaporation of the ether extracts and vacuum sublimation of the residues gave products. Resublimation *in vacuo* gave the samples which were used in analytical determinations.

Deuteration of Sodium Salts.—Excess sodium hydride was suspended in ether in a flask connected to a high vacuum line. Air was removed and an ethereal solution of the decaborane or deuterated decaborane was added in portions through a rubber stopple by means of a hypodermic syringe. The hydrogen produced was vented through the line. After the reaction subsided, the excess sodium hydride was collected on a filter *in vacuo*. Gaseous deuterium chloride was added to the filtrate and the sodium chloride produced was collected on a filter. All operations were conducted *in vacuo*. Removal of the ether and sublimation gave samples of deuterated decaboranes. Analytical samples were obtained by resublimation.

Pyrolysis Method.—Application of a universal method for the determination of hydrogen[15] to the analysis of decaborane has been reported.[16] The method consists of heating a sample to 100° in a sealed platinum, palladium or iron container, and measuring the hydrogen which diffuses through the metal. This method was modified to eliminate sealed metal containers and to allow the use of a normal combustion train leading to a Toepler pump.

The weighed sample of decaborane was put in a bulb on the end of the combustion train. This bulb was cooled in Dry Ice–acetone as the air was pumped out of the system. After the air was removed, a liquid nitrogen bath was used to replace the Dry Ice–acetone and the system was evacuated to a pressure of 3×10^{-4} mm. No loss of decaborane or pick up of moisture was detectable in this operation. The sample was warmed with a heat gun and expanded into the first furnace, which was at a temperature of 850–900°. Pyrolysis to boron and hydrogen occurred immediately and the Toepler pump removed the hydrogen as it formed. When no decaborane could be detected by visual means, the second furnace was heated to 900° to ensure complete decomposition of any residual decaborane or higher boron hydrides. Measurement of the amount of hydrogen produced proved the method to be quantitative and reproducible. The variation was ±0.5%. A typical decomposition requires from 45 minutes to one hour.

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[11] I. Shapiro, M. Lustig and R. E. Williams, THIS JOURNAL, **81**, 838 (1959).

[12] J. van der Maas Reddy and W. N. Lipscomb, *ibid.*, **81**, 754 (1959).

[13] L. F. Fieser, "Experiments in Organic Chemistry," 2nd edition, D. C. Heath and Co., New York, N. Y., 1941, p. 369.

[14] H. C. Brown and C. Grant, THIS JOURNAL, **64**, 2223 (1942).

[15] L. P. Pepkowitz and E. R. Proud, *Anal. Chem.*, **21**, 1000 (1949).

[16] E. L. Simons, E. W. Balis and H. A. Liebhafsky, *ibid.*, **25**, 635 (1953).