off at room temperature. It was not possible to bring the product to reaction with $(NPCl_2)_3$ in triethylamine, ether or benzene; but in diglyme (β,β'-dimethoxy-diethyl ether) the reaction was quite extensive even though the NaC_2H itself seemed nearly insoluble.

Replacement of Chloride by Acetylide.—Ten grams each of $(NPCl_2)_3$ and NaC_2H in 200 ml. of diglyme (previously dried by sodium under reflux for 24 hr.) turned black during ten minutes of stirring at room temperature. After 70 min. the mixture was filtered to remove a solid containing chloride but no phosphorus compounds. The diglyme was distilled from the filtrate, under reduced pressure at 70°. Then the oily residue was placed under high vacuum for 6 hr. at 80°, driving out the last of the diglyme and delivering the unused $(NPCl_2)_3$ as a sublimate. This was identified by the mixed melting point method. The final product was a brown, non-crystalline material which began to decompose near 150°. It proved to be insoluble in benzene, nitrobenzene, carbon tetrachloride, acetone, ethanol or ether, as though it were more highly polymeric than the soluble $(NP)_3$-ring compounds. However, it was redissolved by diglyme, indicating no high degree of cross-linking.

Analysis of the Product.—The brown solid product was analyzed for all components in an effort at interpretation of the reaction.

Chloride.—Two roles played by chloride were indicated by the difference of results when chloride was determined after basic hydrolysis at 100° and after a complete breakdown by the Parr peroxide-nitrate bomb method. In each case the final titration was by the Volhard method. The basic hydrolysis gave 42.1% Cl; the Parr-bomb, 50.5% Cl.

Phosphorus and Carbon.—The sample was destroyed by a boiling mixture of sulfuric, nitric and perchloric acids. The resulting carbon dioxide was drawn off, freed of oxidizing gases by shaking with mercury and measured as a gas; % C, 11.1 ± 0.3. The phosphate now was determined by the molybdate method; % P, 25.9 ± 0.4.

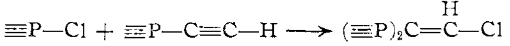
Hydrogen.—It is assumed that no H was removed from C in the acetylide reaction; then from the result for C the % H is calculated as 0.46.

Nitrogen.—The Kjeldahl method gave the % N as 12.18 ± 0.02.

Summary.—Adding the % of the elements here determined gives a total of 100.1 ± 1.2%. If it be assumed that the basic hydrolysis gave all and only the P-bonded chloride, the formula would be written as $[N_3P_{2.88}Cl_{4.10}(C_{3.19}H_{1.59}\text{-}Cl_{0.81})]_x$.

Infrared Spectrum of the Product.—A sample of the acetylide product was pelleted in potassium bromide and the infrared spectrum observed. A medium peak at 871 cm.$^{-1}$, a strong one at 1200 and a weak one at 1990 were essentially the same as for $(NPCl_2)_3$, indicating that the original ring was present. A peak at 3040 was assignable to C–H stretching and another at 770 would be C–H bending. A peak at 1588 would correspond to the literature values for the C=C bond in conjugated systems. The presence of C–C and C=C could not be determined because they would be in a region where the $(NP)_3$ ring produces a wide spectrum without specific peaks.

Interpretation.—The polymerization of a partially acetylided $(NPCl_2)_3$ might occur in at least two ways without disturbing the ring: (1) by the reaction-type



$$\equiv P{-}Cl + \equiv P{-}C{\equiv}C{-}H \longrightarrow (\equiv P)_2C{=}\overset{H}{C}{-}Cl$$

or (2) by direct polymerization of the acetylide unit. The spectroscopically indicated C=C bond would be explained on either basis. The empirical formula suggests some occurrence of (1); however there are too few phosphorus valences available to account for conversion of the 0.81Cl to C–Cl bonds in the manner of (1) alone. Full consistency would seem to require at least a limited occurrence of (2) as well. A full understanding of this polymer might require a more extensive study than is possible within our plans for the future.

LOS ANGELES 7, CALIFORNIA

[CONTRIBUTION FROM THE RESEARCH LABORATORY, OLIN MATHIESON CHEMICAL CORPORATION]

Exchange Sites in the Deuteration of Decaborane

BY I. SHAPIRO, MAX LUSTIG AND ROBERT E. WILLIAMS

RECEIVED AUGUST 1, 1958

The progress of the hydrogen–deuterium exchange between decaborane and deuterium oxide in dioxane has been followed by nuclear magnetic resonance spectroscopy. The most rapid exchange occurs with the bridge hydrogens; slower rates of exchange take place at the terminal sites. The preferential order of terminal hydrogen exchange is (a) two equivalent sites, each adjacent to two bridge positions, (b) four equivalent sites, each adjacent to one bridge position, (c) two apical sites and the two remaining sites located furthest from the bridge positions. When a sample of decaborane is separated from the deuterium oxide after becoming bridge-deuterated and is aged in dioxane, H–D exchange occurs involving only the bridge deuterons and the neighboring hydrogens on the four identical terminal sites. A mechanism accounting for these exchanges is proposed.

Decaborane can be deuterated by exchange with deuterodiborane[1] or with deuterium oxide.[2] In the former case the exchange takes place preferentially at the terminal sites of decaborane while in the latter case there is a rapid exchange in the bridge positions followed by a slower exchange at the terminal sites. In either case the exchange is complicated by interaction[3] or hydrolysis[4] with resultant loss of decaborane.

Since a position analysis of decaborane can be made by nuclear magnetic resonance spectroscopy,[5] this technique was applied to the study of the exchange of decaborane with deuterium oxide. In addition to confirming the previous work,[2] it has been possible to observe the relative rate and preferential order in which deuterium atoms replace the various terminal hydrogen atoms in decaborane.

Experimental

Decaborane was prepared by the pyrolysis of diborane[6] and purified by sublimation in standard high vacuum equipment. Deuterium oxide of 99.5% purity was obtained from Stuart Oxygen Co. Dioxane was purified by distillation.

The B^{11} and proton n.m.r. spectra were obtained with a Varian High Resolution Spectrometer operating at 12.8 and 40 mc., respectively. Mass spectra were obtained with a Consolidated Model 21-103 mass spectrometer operating at 70 volts.

The procedure was similar to that described by other workers.[2] Weighed amounts of decaborane and deuterium oxide were condensed with dioxane to give the following concentrations: $B_{10}H_{14}$, 0.08 *M*; D_2O, 3.10 *M*. These ma-

---

(1) J. J. Kaufman and W. S. Koski, THIS JOURNAL, **78**, 5774 (1956).

(2) M. F. Hawthorne and J. J. Miller, *ibid.*, **80**, 754 (1958).

(3) I. Shapiro and R. E. Williams, Abstracts of Papers of 132nd Meeting, American Chemical Society, New York, N. Y., September 1957, 16-N.

(4) Ref. 2 did not disclose that decaborane also undergoes hydrolysis; in the course of 3 hr. exposure to water in dioxane an appreciable loss in decaborane occurs.

(5) R. E. Williams and I. Shapiro, *J. Chem. Phys.*, **29**, 677 (1958).

(6) I. Shapiro, H. G. Weiss, M. Schmich, S. Skolnik and G. B. L. Smith, THIS JOURNAL, **74**, 901 (1952).

terials were allowed to react with each other for specified lengths of time and followed by quenching the reaction mixtures in liquid nitrogen. The dioxane and remaining (partially deuterated) water were removed by distillation and the decaborane solid sublimed from the partially deuterated boric acid (shown by infrared analysis). For n.m.r. analysis the decaborane was dissolved in carbon disulfide. For mass spectral analysis the decaborane vapor was introduced directly into the mass spectrometer.

Results

The initial H–D exchange takes place at the bridge positions of decaborane as evidenced by the change in the proton n.m.r. spectrum of decaborane. The proton spectrum of decaborane is shown in Fig. 1A; that of decaborane exposed to deuterium oxide in dioxane for 0.15 hr., in Fig. 1B. The normal proton spectrum[7] consists of two displaced quartets (a,b) superimposed upon an unresolved multiplet (c) representing the bridge hydrogens and occurring at the high field side of the spectrum. Each quartet arises from the splitting of terminal protons by the 3/2 spin of B^{11}. The small quartet (a) represents the two apex positions and the large quartet (b) represents the remaining eight terminal protons. Protons associated with B^{10} nuclei (20% abundance) give rise to unresolved septets which lie within the quartet boundaries and contribute some distortion. Replacement of the bridge hydrogens with deuterium causes the disappearance of the broad multiplet bringing each quartet to the common baseline (Fig. 1B). Had there been any gross preferential exchange of the terminal protons within the 0.15 hr. sample, the relative intensity of the two quartets would almost certainly have changed. The fact that the bridge hydrogens, almost alone, took part in the exchange under the experimental conditions described is shown by the B^{11} n.m.r. spectra in which the B^{11} spectrum of the bridge-deuterated decaborane is essentially the same as that of normal decaborane.

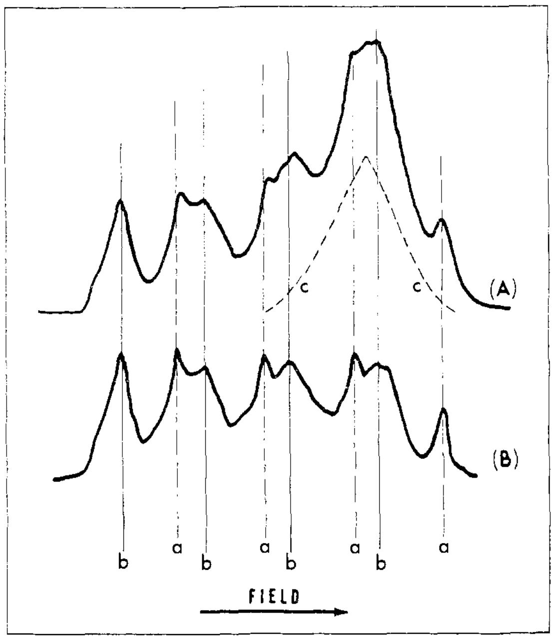


Fig. 1.—Proton n.m.r. spectra of (A) normal and (B) bridge-deuterated decaboranes: a = apical sites, b = all other terminal sites, and c = bridge positions.

As decaborane is exposed to deuterium oxide for increasing lengths of time, the H–D exchange with the terminal hydrogens becomes apparent. A series of B^{11} spectra showing the progressive spectral changes as a function of reaction time are given in Fig. 2. The B^{11} spectrum of isotopically normal decaborane[7] consists of a high field doublet representing the two apical boron positions, and a low field triplet composed of the coincidental overlapping of two doublets. The detailed assignment[5] of the apparent triplet has been made previously by use of perdeuterodecaborane.

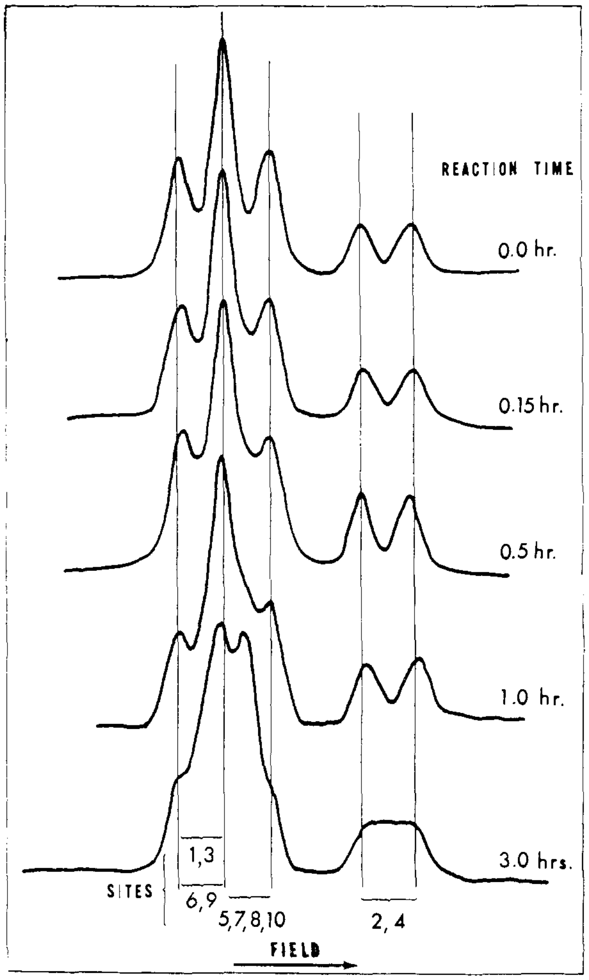


Fig. 2.—B^{11} n.m.r. spectra of decaborane as function of reaction time.

A doublet in the B^{11} spectrum of decaborane arising from a B^{11}–H unit would collapse into a singlet (unresolvable triplet) if the hydrogen were replaced by a deuterium atom.[5] In comparing the spectra of Fig. 2 the vertical amplitudes are not significant since they are dependent upon relative concentration and geometry of the decaborane samples and signal attenuation. All spectra were taken at one set operating speed so that the relative position of the peaks with respect to field strength (horizontal axis) would be on the same

---

(7) J. N. Shoolery, *Disc. Faraday Soc.*, **19**, 215 (1955).

scale. Since each timed experiment was carried out separately, no effort was made to duplicate the exact concentration of the treated decaborane in the carbon disulfide. As in methylene chloride,[2] there is no rearrangement of protons or deuterons in decaborane when dissolved in carbon disulfide.

In order to discuss the H–D exchange of the terminal hydrogens, each boron atom in decaborane has been assigned a number[8] as indicated in Fig. 3.

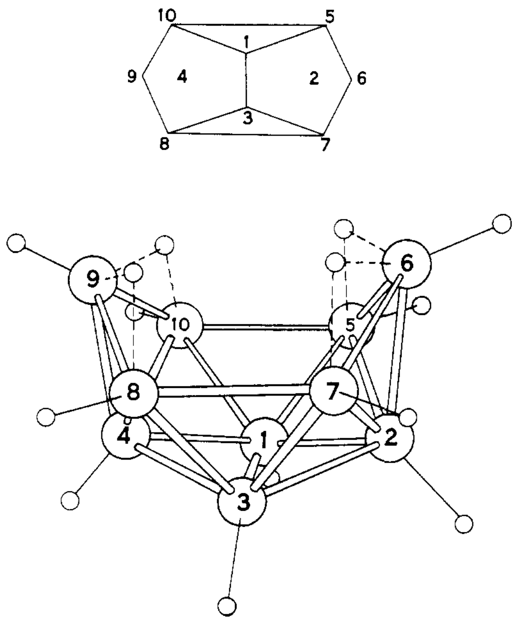


Fig. 3.—Numbering of sites in decaborane molecule.

In the B^{11} spectrum of normal decaborane the doublet occurring at highest field corresponds to apex sites 2 and 4; the doublet at the high field side forming half the triplet represents sites 5, 7, 8, 10; the remaining doublet, low field side of the triplet, results from two superimposed doublets, sites 1, 3 and 6, 9.[5] From Fig. 2 the preferential order of terminal hydrogen exchange obtained by the relative rate of collapse of the various doublets appears to be related to the accessibility of the bridge hydrogens, *viz.*, 6, 9; 5, 7, 8, 10; 2, 4; and 1, 3. The two most electropositive groups (less electron shielding), *viz.:* 1, 3 and 6, 9, have been placed at opposite ends of this order. These assignments (1, 3 and 6, 9) have been selected because of steric considerations as well as the proposed mechanism described under Discussion which also seems to apply to other reactions.

The aging of the 0.5 hr. sample in pure dioxane produces changes in its B^{11} n.m.r. spectrum as shown in Fig. 4. The primary effect with time was a collapse at sites 5, 7, 8, 10, indicating that only these sites were participating in the H–D exchange with the bridge positions. Longer exposure times, up to 120 hr., did not result in further changes in the spectrum. No evidence of decaborane decomposition was observed.

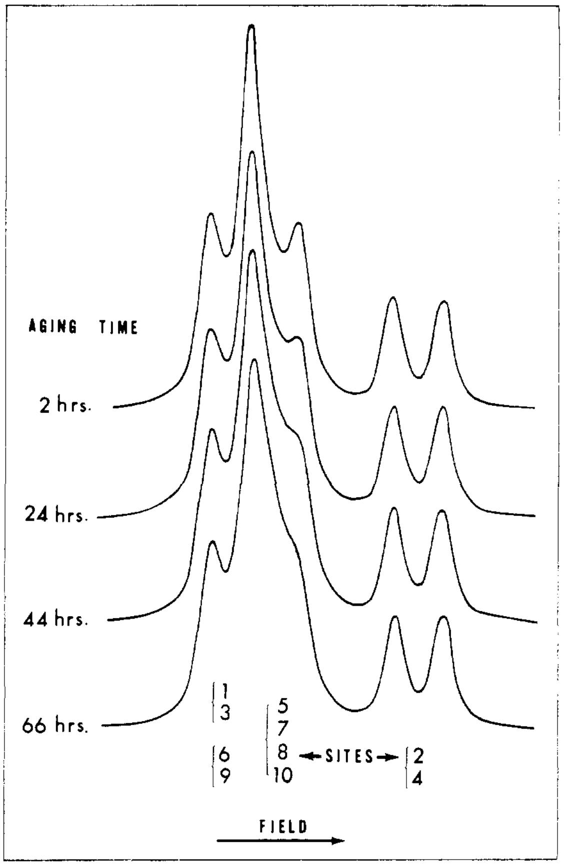


Fig. 4.—Change in B^{11} n.m.r. spectrum upon aging of the 0.5 hr. sample in dioxane.

The contours of the spectra of Fig. 2 also have been correlated with the number of deuterium atoms present in each sample as determined by mass spectral analysis. Figure 5 shows the polyisotopic mass spectra (above *m/e* 110) for the various deuterated decaborane samples. The maximum discernible number of deuterium atoms can be deduced from the largest mass number occurring in the corresponding mass spectrum. For example, the "cut-off peak" for decaborane occurs at *m/e* 124, corresponding to the species $B^{11}{}_{10}H_{14}$; for perdeuterodecaborane, 138, corresponding to $B^{11}{}_{10}D_{14}$. The 0.15 hr. sample contains an observable maximum of four deuterium atoms known to be located in the bridge positions. The 3 hr. sample had an observable maximum of 10 deuterium atoms. The calculation of the distribution of the partially deuterated species from the mass spectra is complicated somewhat by the difference in fragmentation of bridge and terminal hydrogens (or deuteriums). The monoisotopic spectrum of normal decaborane indicates fragmentation of hydrogens occurs essentially in pairs for the first six hydrogens.[9] A preliminary examination of the mass spectrum for the bridge deuterated sample indicates that a high proportion of these pairs consists of one terminal proton and one bridge deuteron. The technique of selective exchange should allow

---

(8) This numbering system is the one accepted by the Boron Nomenclature Committee as described by G. Schaeffer, Abstracts of papers of the 133rd Meeting of the American Chemical Society, San Francisco, April, 1958, 2-L.

(9) I. Shapiro, C. O. Wilson, J. Ditter and W. J. Lehmann, Abstracts of 133rd Meeting of the American Chemical Society, San Francisco, April, 1958, 39-L.

a better understanding of the mass spectral fragmentation patterns of the boron hydrides.

Discussion

Although the hydrolysis of decaborane complicates the system within which the H–D exchange takes place, it is expected that the exchange mechanism can be developed independently of the hydrolysis reaction; the n.m.r. spectra reported here were obtained from decaborane recovered from the reaction mixture. Other studies at this Laboratory have shown the initial reaction rate in the hydrolysis of decaborane to be slow with respect to subsequent rate of hydrolysis of its intermediates. Thus, if intermediates (however short-lived) did partake in the "over-all" exchange, such effects would be secondary.

The exchange mechanism proposed here is a Lewis acid–base type reaction involving several discrete steps. The first step is an equilibrium complex formation in which the Lewis base, water or dioxane, attaches to the 6 and/or 9 boron sites, which are the most acidic (electropositive) sterically available positions within the molecule. Should the base attack occur at the 1 or 3 position, the following modes of exchange would not be expected to take place. The donation of a pair of electrons by the oxygen (base) to the 6 or 9 boron atoms satisfies the boron electronically, without the necessity of sharing in one bridge-hydrogen electron pair thus allowing that hydrogen to occupy a temporary terminal position upon the neighboring boron atom (5, 7, 8 or 10). During this oscillation the former bridge proton might well participate in a very rapid (perhaps ionic) exchange with deuterium oxide, thus accounting for a rapid bridge exchange. During the time the bridge deuterium occupies the terminal position, it differs geometrically from the normal terminal proton. Since these positions are different, exchange can occur either while neighbors on the boron atom or while restoring the bridge position. This exchange is slower than the bridge exchange.

Whenever the base which attacks at the 6- or 9-positions of decaborane is deuterium oxide or deuteroxide ion, the proton on the boron is in close proximity to the deuteron (deuterons) on the oxygen, hence H–D exchange might well occur. This exchange is intermediate in rate between the bridge exchange and the "5, 7, 8, 10" exchange and accounts for deuteration of the 6,9-positions. Thus, in the aging process where there is dioxane but no water present, there is no exchange in the 6- or 9-positions; however, the migration of deuterium in the bridge positions to the 5-, 7-, 8-, 10-positions, dioxane serving as the base, can still take place. Exchange involving the 1,3- and 2,4-positions does not occur in dioxane alone but does take place in the presence of water.

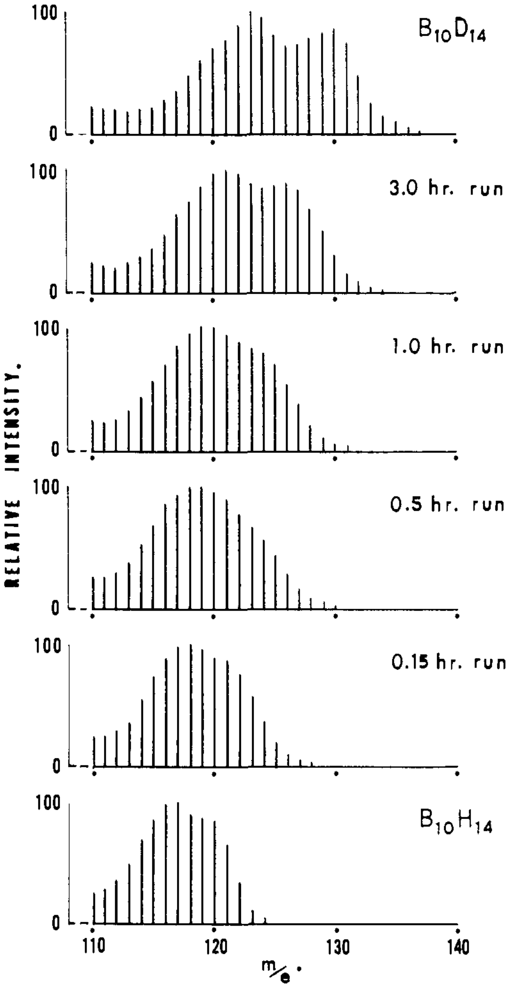


Fig. 5.—Comparison of the partially deuterated decaboranes with normal decaborane and completely deuterated decaborane.

From previous work[5] with perdeuterodecaborane it was established that the low field doublet of the apparent triplet in the B^{11} n.m.r. spectrum of decaborane is the composite of the 1,3 and 6,9 doublets and that these doublets are not exactly superpositioned. Examination of the spectra in Fig. 2 reveals that although the 5,7,8,10 doublet collapsed upon deuteration into its expected center, the deuterated portion of the 1,3-6,9 doublet did not appear at the "composite" center. The interpretation is made that essentially only one of these doublets collapsed. From the above discussion the collapsed doublet has been assigned to the 6,9 sites.

PASADENA, CALIFORNIA