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A Deuterium-Exchange Study on the $B_9H_{14}^-$ Ion

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With the aid of selective deuterium labeling, the ^{11}B nmr spectrum of $B_9H_{14}^-$ has been completely assigned on the basis of a 5340 topological structure. In weakly acidic deuterium oxide the 4,6,8 terminal hydrogens exchange with the solvent. In neutral water exchange with the solvent does not occur, although bridge and 4,6,8 terminal hydrogens scramble slowly by what is probably an intramolecular process. In weakly basic deuterium oxide the bridge hydrogens rapidly exchange, while in strong base both bridge and 4,6,8 terminal positions deuterate. With the use of deuterium-labeled KB_9H_{14} the ^{11}B nmr spectrum of isononaborane(15) has also been assigned and an exchange process between bridge and terminal hydrogens has been detected. Possible mechanisms for these reactions are discussed.

Introduction

Isotope-exchange reactions are a powerful tool for the study of the dynamic behavior of molecules. Although many boron hydrides have been shown to undergo isotope exchange under a wide range of conditions, only decaborane(14) has been studied in detail in solution.

Dupont and Hawthorne[2] found that decaborane(14) exchanges its apical 1,2,3,4 terminal hydrogens with deuterium chloride in carbon disulfide solution in the presence of aluminum chloride. The bridge hydrogens of decaborane(14) have been found to exchange readily with deuterium oxide owing to their acidic character.[3] The bridge exchange is accompanied by slow base-catalyzed intramolecular exchange between the bridge and the 5,7,8,10 terminal hydrogens. The course of the intramolecular exchange depends on the nature of the solvent. In anhydrous dioxane only the 5,7,8,10 terminal hydrogens exchange with the bridge positions; in the presence of deuterium oxide both the 6,9 and the 5,7,8,10 terminal positions deuterate.

Shapiro, Lustig, and Williams[4] suggested that this exchange proceeds by attack of the base (dioxane) on the 6,9 boron atom, causing the bridge hydrogen to occupy temporarily a terminal position on the neighboring 5,7,8,10 boron. If the attacking base is deuterium oxide or deuterioxide ion, the 6,9 terminal proton is in close proximity to the deuteron(s) on oxygen, and intermolecular exchange may also occur. Intramolecular migration of deuterium does not occur in a nonbasic solvent like methylene chloride.[3]

This paper describes the results of a study of the isotope-exchange reactions of $B_9H_{14}^-$ in deuterium oxide solution. We have also used the deuterium-labeled $B_9H_{14}^-$ from these experiments to assign the ^{11}B nmr spectrum of isononaborane(15) and detect a bridge–terminal exchange process in this molecule.

Experimental Section

General Data.—The ^{11}B nmr spectra were obtained using a Varian DP-60 spectrometer operating at 19.3 MHz. The ^1H spectra were obtained using both Varian DP-60 and A-60 instruments. All ^{11}B chemical shifts are in ppm relative to diethyl ether–boron trifluoride. The magnetic field strength increases from left to right in all spectra. The deuterium oxide solutions of sodium deuterioxide were prepared by the decomposition of sodium peroxide in commercially obtained deuterium oxide (99.7% D_2O). Stock solutions were approximately 2 *N*. Deuterium chloride was prepared by the reaction of phosphorus trichloride and deuterium oxide and was purified by high-vacuum methods. Deuterium oxide solutions of deuterium chloride were obtained by condensing a measured amount of deuterium chloride onto sufficient deuterium oxide to afford an approximately 1 *N* solution. The 1,2,3,4-$B_{10}H_{10}D_4$ was prepared by the aluminum chloride catalyzed reaction of deuterium chloride with decaborane(14) in carbon disulfide.[2]

Procedure.—Typically a weighed sample of KB_9H_{14}[5] was dissolved in sufficient deuterium oxide to ensure good exchange, and either deuterium chloride or sodium deuterioxide was added to achieve appropriate reaction conditions. A sample of the solution was then transferred to an nmr tube, and the exchange was monitored by ^{11}B or ^1H nmr.

Analytical samples of the deuterated compound were isolated by addition of a concentrated deuterium oxide solution of cesium chloride to the reaction mixture. The precipitated cesium salt was filtered, washed twice with ice-cold deuterium oxide, and dried under high vacuum. Deuterium analyses were performed by Josef Nemeth, Urbana, Ill.

Isononaborane(15) Nmr.—Solutions of deuterium-labeled KB_9H_{14} were prepared as described, brought to neutrality, and freeze-dried to isolate the solid product. The samples were then converted to isononaborane(15) by treatment with excess hydrogen chloride at −78° in an nmr reaction tube.[6] The unreacted hydrogen chloride was removed at −78° and approximately 1 ml of toluene was condensed into the tube. The vessel was then inserted into the nmr probe, which had been cooled to the desired temperature, and the spectrum was run with as little delay as possible.

Results

Structure of $B_9H_{14}^-$.—Although the structure of $B_9H_{14}^-$ has not been established by X-ray crystallography, chemical evidence[7] strongly argues for a boron skeleton similar to that found in $B_9H_{13}(NCCH_3)$.[8] Lipscomb[9] has suggested a 2613 topological structure[10]

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[10] For a discussion of the topological theory of boron hydride structures see ref 9, Chapter 2.

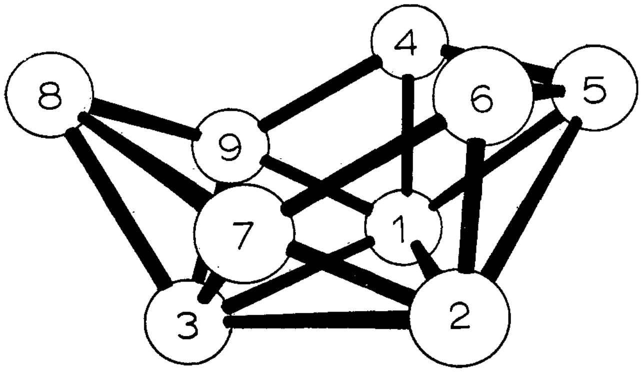

Figure 1.—Boron skeleton and numbering for $B_9H_{14}^-$ and i-B_9H_{15}.

for $B_9H_{14}^-$ derived by replacing the acetonitrile ligand of $B_9H_{13}(NCCH_3)$ with a hydride ion. Figure 1 shows this B_9 framework; the ligand in $B_9H_{13}(NCCH_3)$ is attached to B-8. The boron skeleton of decaborane(14) may be generated by joining the tenth boron atom to the 4,5,6 positions.

The ^{11}B nmr spectrum of an aqueous solution of KB_9H_{14} (Figure 2A) consists of two slightly overlapping doublets (J = 133 Hz for both) in 1:2 ratio at +7.6 and +23.3 ppm, respectively. The spectrum is clearly inconsistent with a proton arrangement derived from $B_9H_{13}(NCCH_3)$, which requires three BH_2 groups, and suggests a 5340 topological structure. The presence of five bridge hydrogens is confirmed by the deuterium analysis of the bridge-labeled ion (see below).

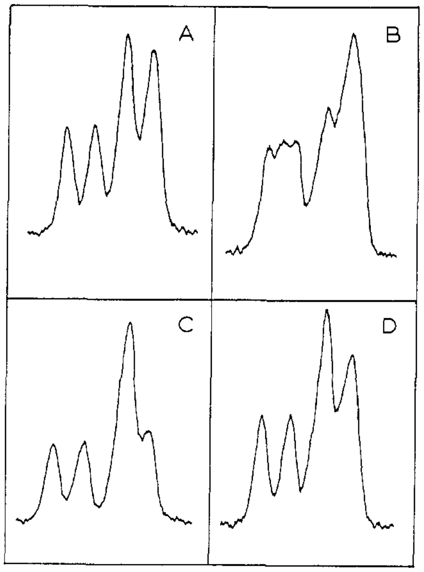

Figure 2.—The ^{11}B nmr spectra of $B_9H_{14}^-$: (A) $B_9H_{14}^-$; (B) ion prepared from 1,2,3,4-$B_{10}H_{10}D_4$; (C) 4,6,8-$B_9H_{11}D_3^-$, acid-catalyzed exchange; (D) μ-$B_9H_9D_5^-$ after 4 hr in H_2O.

The structure of $B_9H_{14}^-$ is closely related to that of isononaborane(15)[5] (proposed 6330 topology). The apparent threefold symmetry of the boron framework and equivalence of the five bridge hydrogens implied by the nmr spectrum is reminiscent of the case of the $B_{11}H_{14}^-$ ion[11] and may arise from a facile tautomerism among the bridge hydrogens.

Assignment of the Nmr Spectrum.—The ^{11}B nmr spectrum of $B_9H_{14}^-$ is assigned unambiguously by comparing the spectrum of the ion prepared from 1,2,3,4-$B_{10}H_{10}D_4$ with that of the acid-catalyzed $B_9H_{14}^-$ exchange product (Figures 2B and 2C, respectively). Generation of $B_9H_{14}^-$ from decaborane(14) with deuterium on the apical 1,2,3,4 borons should give rise to a product completely labeled at the 1,2,3 borons and only one-third labeled at the 5,7,9 positions, assuming the deuterium label neither exchanges nor randomizes during the degradation. From Figure 2B it is evident that neither exchange nor randomization has occurred and that the partially collapsed low-field doublet may be assigned to the 5,7,9 borons, while the upfield resonance results from the combined signals from the 4,6,8 and the 1,2,3 borons. The observed coupling constant of 133 Hz for the high-field doublet should therefore be regarded as an approximate value. Comparison of the shapes of the high-field portion of the spectrum in Figures 2B and 2C leads to the conclusions that acid-catalyzed exchange results in deuteration of the 4,6,8 positions and that the resonance arising from the 1,2,3 borons occurs at slightly higher field than that of the 4,6,8 borons.

The proton spectrum of $B_9H_{14}^-$ is presented in Figure 3A. Two sets of terminal proton resonances, a and b, may be distinguished in addition to the bridge proton resonance c at highest field. Comparison of this spectrum with that of the acid-catalyzed exchange product (Figure 3B) allows the assignment of resonance b to the 4,6,8 terminal protons and resonance a to the combined signals from the 1,2,3 and 5,7,9 terminal positions.

Acid-Catalyzed Exchange.—The ^{11}B nmr spectrum of $B_9H_{14}^-$ in approximately 10^{-3} N deuterium chloride changes within 20 min to that shown in Figure 2C. As outlined above, this indicates deuteration of the 4,6,8 positions. The proton spectrum of this solution indicates that the bridge hydrogens do not exchange under these conditions; however, over a period of several hours at room temperature, the bridge region of the spectrum gradually collapses indicating very slow exchange of the bridge hydrogens by a secondary process (Figure 3B). *Anal.* Calcd for $CsB_9H_{11}D_3$: D, 21.4. Found: D, 23.8.

Neutral Deuterium Oxide.—The ^{11}B and ^1H nmr spectra of $B_9H_{14}^-$ in neutral deuterium oxide do not change detectably over an 8-hr period; after 15 hr at room temperature the bridge portion of the proton spectrum diminishes slightly in relative intensity. Hence, no appreciable exchange occurs in neutral solution over reasonably short periods of time.

Exchange in Weak Base.—The ^{11}B nmr spectrum of a solution of KB_9H_{14} in approximately 10^{-3} N sodium deuterioxide is identical with that shown in Figure 2A. The ^1H nmr spectrum (Figure 3C) shows complete exchange of the bridge hydrogens. This exchange is very fast, since the bridge resonance had always disappeared in the interval between the initial mixing of the solution and the first scan of the nmr spectrom-

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[11] V. D. Aftandilian, H. C. Miller, G. W. Parshall, and E. L. Muetterties, *Inorg. Chem.*, **1**, 734 (1962).

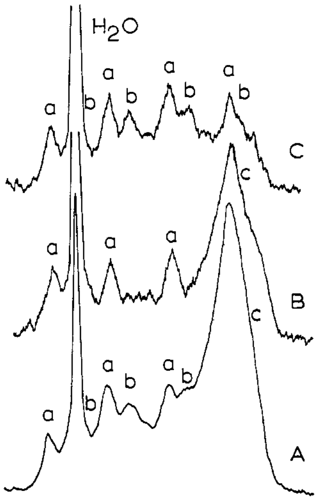


Figure 3.—The ^{1}H nmr spectra of $B_9H_{14}^-$: (A) $B_9H_{14}^-$; (B) 4,6,8-$B_9H_{11}D_3^-$; (C) μ-$B_9H_9D_5^-$.

eter (2–3 min). *Anal.* Calcd for $CsB_9H_9D_5$: D, 35.7. Found D, 35.7.

Exchange in Strong Base.—As demonstrated by the ^{11}B nmr spectrum, the 4,6,8 terminal protons undergo complete exchange within 10 min in 1 *N* sodium deuterioxide solution. The proton spectrum shows the expected absence of the signals arising from the 4,6,8 and bridge protons. *Anal.* Calcd for $CsB_9H_6D_8$: D, 57.1. Found: D, 51.2.

The deuterium analysis implies a composition of $CsB_9H_{6.8}D_{7.2}$. Although the deuterium content is slightly low, the evidence furnished by the nmr leaves little doubt as to the identity of the product.

Bridge–Terminal Exchange in $B_9H_{14}^-$.—The behavior of a solution of μ-$KB_9H_9D_5$ in neutral protium oxide was monitored by ^{11}B nmr. Initially the spectrum was identical with Figure 2A, but within 3–4 hr it became evident that deuterium was appearing in the 4,6,8 positions (Figure 2D). Only these sites participate in the exchange.

Boron-11 Nmr Spectrum of Isononaborane(15).—The ^{11}B nmr spectrum of a toluene solution of isononaborane(15) at −50° is shown in Figure 4A. The spectrum is basically similar to that of $B_9H_{14}^-$; the broad low-field doublet is half the intensity of the high-field signal, which consists of two overlapping equal-intensity doublets. Unambiguous assignment is achieved by examining the spectrum of isononaborane(15) prepared from 1,2,3,5-$KB_9H_{10}D_4$ (Figure 4B). Clearly the lowest field resonance arises from the 5,7,9 borons, and the 1,2,3 borons give rise to the middle doublet. This assignment is confirmed by the spectrum of isononaborane(15) prepared from 4,6,8-$KB_9H_{11}D_3$ (Figure 4C), which shows collapse of the highest field portion of the spectrum.

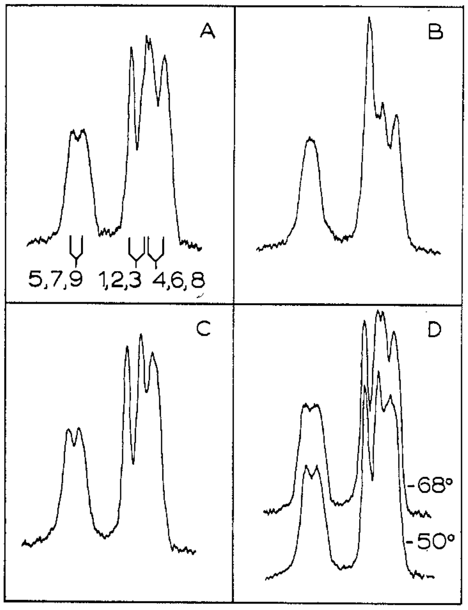
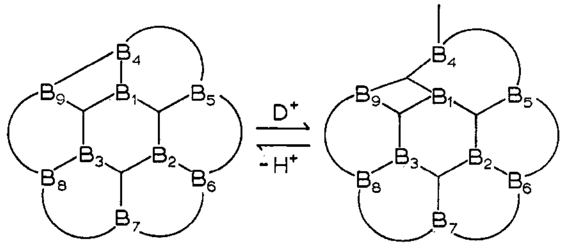


Figure 4.—The ^{11}B nmr spectra of *i*-B_9H_{15} in toluene: (A) *i*-B_9H_{15}; (B) compound prepared from 1,2,3,5-$KB_9H_{10}D_4$; (C) compound prepared from 4,6,8-$KB_9H_{11}D_3$; (D) compound prepared from μ-$KB_9H_9D_5$.

Bridge–Terminal Exchange in Isononaborane(15).—When the nmr probe temperature was increased from −65 to −50°, the collapsed high-field portion of the spectrum of the sample shown in Figure 4C partially and irreversibly resolved to show doublet structure. To confirm the possibility of exchange between bridge and 4,6,8 terminal hydrogens suggested by this observation, an nmr sample of isononaborane(15) was prepared from μ-$KB_9H_9D_5$ and deuterium chloride. The ^{11}B nmr spectrum of a toluene solution of this material at −68° (Figure 4D) is virtually identical with that of the deuterium-free compound (Figure 4A). When the sample was warmed to −50° in the nmr probe, the high-field doublet collapsed to a singlet (Figure 4D) indicating migration of deuterium to the 4,6,8 terminal positions. This spectrum did not change when the sample was recooled to −68°, nor did the 5,7,9 or the 1,2,3 doublets show any sign of collapse.

Discussion

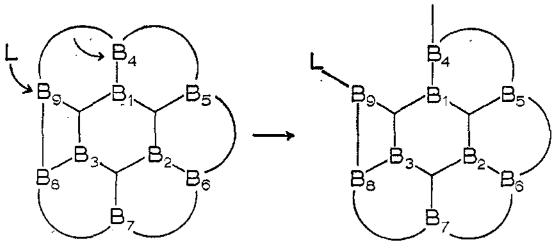
Acid-Catalyzed Exchange.—A reasonable pathway for exchange in acid solution is addition of a deuteron to a terminal position on a 4,6,8 boron to form a neutral $B_9H_{14}D$ intermediate followed by subsequent loss of a proton from this BHD group (eq 1). It is interesting to note that the neutral $B_9H_{14}D$ implied by eq 1 necessarily has a hydrogen atom arrangement different from that proposed for isononaborane(15),[5] although the boron skeletons should be nearly identical.



(1)

It is somewhat surprising that the 5,7,9 terminal hydrogens do not exchange in either acidic or basic deuterium oxide. A possible explanation may be that addition of an axial proton to a 5,7,9 boron to form a BH_2 group results in greater crowding with the bridge hydrogens than protonation of a 4,6,8 position.

Bridge–Terminal Exchange in $B_9H_{14}^-$.—The course of the scambling between bridge and 4,6,8 terminal hydrogens is probably similar to the intramolecular bridge migration in decaborane(14),[3,4] although an intermolecular process cannot be excluded on the basis of this study. The intramolecular exchange might begin with attack by a donor water molecule on a 5,7,9 boron followed by a shift of the associated bridge deuterium to an adjacent 4,6,8 boron to form a BHD group. Such an intermediate is related to the hypothetical 4342 $B_9H_{15}^{2-}$ (eq 2). The slow appearance of deuterium in bridge positions in acidic deuterium oxide probably also occurs by this process.



(2)

Base-Catalyzed Exchange.—A probable mechanism for bridge exchange in weakly basic deuterium oxide involves removal of a slightly acidic bridge proton by a deuterioxide ion to form a doubly charged $B_9H_{13}^{2-}$ intermediate (eq 3).

$$B_9H_{14}^- + OD^- \longrightarrow [B_9H_{13}^{2-}] + HDO \qquad (3)$$
$$[B_9H_{13}^{2-}] + D_2O \longrightarrow \mu\text{-}B_9H_{13}D^- + OD^-$$

The exchange of both bridge and 4,6,8 terminal hydrogens in strongly basic deuterium oxide has no parallel in the known reactions of decaborane(14). One possible course is direct removal of protons from both sites by deuterioxide ion under highly alkaline conditions, but a more satisfying explanation might simply be an enhanced rate of intramolecular exchange brought about by the high concentration of the more nucleophilic deuterioxide ion.

Bridge–Terminal Exchange in Isononaborane(15).—Exchange of bridge and terminal hydrogens is established for a few of the more labile boron hydrides such as tetraborane(10),[12] although little is known about the details of these processes. It is somewhat curious that only the 4,6,8 terminal hydrogens appear to participate in exchange with the hydrogen bridges in isononaborane(15). Unfortunately the experiments described in this paper shed little light upon how this process occurs, or even whether the reaction is inter- or intramolecular. At the present time there is little basis for speculation on this interesting phenomenon.

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Proton Magnetic Resonance Study of Aluminum(III) Chloride in Water–Dimethyl Sulfoxide Solvent Mixtures

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In water–dimethyl sulfoxide solvent mixtures the aluminum(III) ion is preferentially solvated by water at water mole fractions approximately equal to 0.80 or greater and by dimethyl sulfoxide at water mole fractions approximately equal to 0.75 or less. Evidence is presented that bonding water molecules donate more charge to the central aluminum(III) ion in the solvated $Al(DMSO)_n(H_2O)_{6-n}{}^{3+}$ ion than do bonding dimethyl sulfoxide molecules. Measurements of the rate of exchange of dimethyl sulfoxide molecules between coordinated and bulk solvent sites suggest that dimethyl sulfoxide molecules can exchange by two mechanisms: direct exchange of dimethyl sulfoxide molecules between bulk and coordinated sites at mole fractions of water less than 0.75 and indirect exchange of dimethyl sulfoxide molecules by replacement of dimethyl sulfoxide by water followed by replacement of water by dimethyl sulfoxide at mole fractions of water approximately equal to 0.8 and greater. Measurement of the water–proton exchange rates gave an apparent first-order rate constant with a hydrogen ion concentration dependence given by $k_{app} = k_1[H^+] + k_2/[H^+]$. The existence of the acid-catalyzed path is consistent with the results of Swift and coworkers for hydrated cations in aqueous media. The path dependent on $[H^+]^{-1}$ is consistent with the mechanism postulated by Fong and Grunwald for aqueous solutions of $AlCl_3$.

The solvation of aluminum(III) in various solvents has received considerable attention. The use of nuclear magnetic resonance techniques has given the value of 6 for the primary solvation number, *i.e.*, the number of solvent molecules in the first coordination shell, of aluminum(III) in water,[1–3] in dimethyl sulfoxide[4] (DMSO), in dimethylformamide[5,6] (DMF), and in ammonia.[7] In water–acetone, water–dioxane, wa-

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