charge-transfer transition moves from the infrared region (9000 cm^{-1}) for PR_3 and AsR_3 toward the uv region for Et_2S and pyridine. The halogen transitions remain unchanged throughout this process. The energy of the L → M transiton parallels the reducing power of the ligand and we suggest that this may reflect the energy of the L σ-bond orbitals relative to the metal. Furthermore, we feel that the formation of high-energy orbitals with consequent low-lying excited states in the case of the phosphines and arsines may be responsible for the "softness" of these ligands particularly since little evidence for π bonding from these can be found experimentally.

Acknowledgments.—We wish to thank Drs. G. J. Leigh and D. M. P. Mingos for the gift of the compounds and the Science Research Council for financial support and for studentships to R. G. and M. D. R. We also acknowledge helpful discussions with Dr. Leigh, Dr. J. F. Nixon, and Professor M. F. Lappert.

CONTRIBUTION NO. 2129 FROM THE DEPARTMENT OF CHEMISTRY,
INDIANA UNIVERSITY, BLOOMINGTON, INDIANA 47401

Intramolecular Hydrogen Exchange in Tetraborane(10)[1]

BY RILEY SCHAEFFER* AND LARRY G. SNEDDON

Received January 20, 1972

Intramolecular hydrogen exchange in tetraborane(10) has been studied by utilizing isotopic labeling in conjunction with high-field nmr. Both qualitative and quantitative evidence, obtained by studying the scrambling reactions of μ-B_4H_9D and μ-B_4D_9H, has established that intramolecular hydrogen exchange proceeds at two different rates. The faster exchange involves the bridge and four terminal positions while the slower exchange involves the bridge and the remaining two terminal positions. Further evidence established that the two unique terminal protons which were exchanging at the slower rate are attached to the 2,4 boron atoms. Rate data are presented for both exchanges and possible mechanisms of exchange are discussed. The gas-phase intermolecular exchange reaction of B_4H_{10} and B_2D_6 was reinvestigated, since it had previously been suggested that the 1,3 terminal positions exchange faster than the other positions in tetraborane(10). No evidence was found to support this suggestion.

Introduction

Slow intramolecular hydrogen exchange was first noted in tetraborane(10) by observing the ir spectrum *vs.* time of tetraborane(10) which had been partially deuterated in the terminal positions.[2,3] A scrambling of the deuterium from the terminal to bridge positions was observed. Similar studies with the isotopically labeled compounds, μ,1-dideuteriotetraborane(10)[4] and μ-deuteriotetraborane(10)[5] confirmed that slow intramolecular exchange involving the interconversion of bridge and terminal positions was taking place. In each study only qualitative information about exchange rates could be obtained and nonpreferential scrambling was assumed.

Further evidence for an intramolecular type of exchange in tetraborane(10) was found in the zero source contact mass spectral analysis[6] of the specifically labeled compound, μ-$^{10}B_4H_9D$. The spectrum of the scrambled material was found to be unchanged from that of the labeled material which is inconsistent with an intermolecular type of scrambling mechanism.

The introduction of new nmr spectrometers operating at higher field strengths than previously attainable now permits proton and deuterium nmr spectra to be a useful tool for the boron chemist. We have therefore applied these techniques to investigate intramolecular exchange in tetraborane(10).

Experimental Section

Preparation of Samples.—The standard high-vacuum techniques used in this investigation are described elsewhere.[7]

Lithium aluminum deuteride (isotopic purity >99.5%) was obtained from Metal Hydrides, Inc. Deuterium oxide was obtained from the Atomic Energy Commission and was used without further purification.

Isotopically enriched diborane, B_2D_6, was prepared by the reduction of $BF_3 \cdot O(C_2H_5)_2$ with $LiAlD_4$. Normal diborane, $^{n}B_2H_6$, and tetraborane(10), $^{n}B_4H_{10}$, were obtained from laboratory supply. Pentaboranes(11) were prepared in a hot-cold circulating system described elsewhere.[8]

Isotopically labeled tetraboranes(10), μ-B_4H_9D and μ-B_4D_9H, were prepared by cleavage of B_5H_{11} and B_5D_{11} with D_2O and H_2O, respectively.[5] Tetraborane(10) labeled with an ^{11}B in the 4 position was prepared as reported.[4]

Spectroscopic Techniques.—Nuclear magnetic resonance spectra were obtained with a Varian Associates HR-220 spectrometer equipped with standard Varian variable temperature probe accessories. Multiple scans were obtained using the Varian Associates 1024 time averaging computer. Proton, deuterium, and boron spectra were obtained at 220 MHz, 33.1 MHz, and 70.6 MHz, respectively. In each case special care was taken to avoid saturation effects.

Procedure.—Scrambling reactions were carried out in the liquid phase in standard medium wall precision nmr tubes.

For each data point the nmr tube was placed into a slush bath and timing started 15 sec after immersion. After an appropriate time interval the nmr tube was removed and quenched at −196° to stop the reaction. To prevent further scrambling while the spectrum was taken, the nmr probe was cooled below −10°. Normally 16 sweeps were accumulated at each point with the aid of a time averaging computer. The time averaged spectrum was then printed and subsequently integrated by weighing. The nmr tube was then removed from the probe and the above procedure repeated. At various intervals a wider sweep width

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[1] Studies of Boranes XXXIII; for paper XXXII of this series see L. G. Sneddon and R. Schaeffer, *Inorg. Chem.*, **11**, 3102 (1972).

[2] J. E. Todd and W. S. Koski, *J. Amer. Chem. Soc.*, **81**, 2319 (1959).

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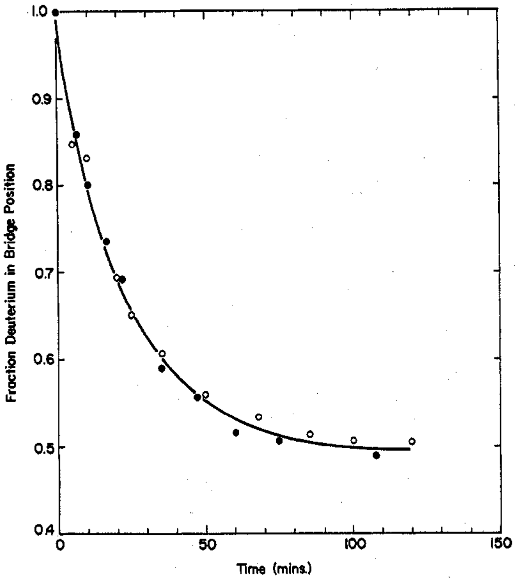

Figure 1.—Typical data curves of μ-B_4H_9D scrambling reactions at 19.0°.

was selected to check for resonances arising from any decomposition products. The temperatures for the reactions 5.5° (benzene slush), 11.8° (*p*-dioxane slush), 19° (acetophenone slush), and 22.5° (water at room temperature) are believed to be accurate to $\pm 0.5°$.

Mass spectra were obtained on the CH-7 mass spectrometer of selected samples before and after scrambling had occurred. Within experimental error, no difference in the mass spectrum was observed which is in agreement with previous results.[6]

Calculations.—All calculations were made on the CDC 6600 computer.

Solutions of the rate equations for the various models tested were found with a computer program obtained from McLaughlin and Rozett of Fordham University. This program can treat kinetic situations linking up to four components by first-order reversible reactions. The above program was modified to be compatible with the available subroutine STEPIT,[9] a program capable of curve fitting.

The general procedure for curve fitting was to guess initial values of the rate constants, calculate a theoretical curve (decrease in bridge deuterium concentration *vs.* time), and compare the residuals obtained at each data point with the residuals obtained when the procedure was repeated with the rate constants varied slightly. Several different initial guess values were utilized for each model to test for false minima.

The results obtained from the calculations above for the first rate constant were compared with the results obtained by treating the initial data in Figure 1 as a simple first-order equilibrium reaction involving the bridge and four terminal positions.

For the general case

$$\mathrm{A} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{B}$$

it can be shown[10] that the rate equation can be integrated to give the expression

$$\ln \frac{A_0 - A_e}{A_0 - A_e} = (k_1 + k_{-1})t$$

where A_0 = initial concentration of A, A_e = equilibrium concentration of A, and A = experimentally determined concentration at time *t*.

The boron scrambling reaction of $4\text{-}^{11}B^{10}B_3H_{10}$ was also treated using this equation. In both cases a general least-squares program was used to obtain a satisfactory fit.

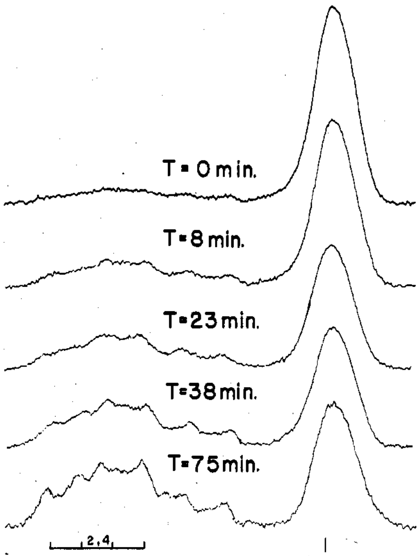

Figure 2.—Dmr (33.8 MHz) of μ-B_4H_9D scrambling reaction.

B_4H_{10}–B_2D_6 Exchange Reaction.—Several experiments were performed with conditions duplicating those used previously.[2,3] In a typical experiment B_4H_{10} (30 mm) and B_2D_6 (100 mm) were placed in a 500-ml reaction flask and warmed to 45° in a constant temperature bath. Reaction times of 10, 30, and 45 min were used, after which the reaction was quenched to −196°. The tetraborane(10) was then purified and sealed into an nmr tube.

Two additional exchange reactions were carried out in the liquid phase by sealing the reactants into nmr tubes which were then warmed to −30° and 0°, respectively.

Due to the low concentrations of deuterium present in the exchanged tetraborane(10) it was necessary to obtain 64 scans using the time average computer before satisfactory spectra could be obtained.

Results

Typical experimental curves representing the decrease in bridge deuterium concentration *vs.* time for μ-deuteriotetraborane(10), μ-B_4H_9D, are presented in Figure 1. Previous ir studies of the scrambling reaction of μ-B_4H_9D had assumed nonpreferential scrambling of deuterium from bridge to terminal positions. However, when we treated the data in Figure 1 as a simple first-order equilibrium between bridge and terminal positions, a satisfactory fit could not be obtained. Typical deuterium spectra from which the data in Figure 1 were obtained are presented in Figure 2. Preliminary examination of these spectra suggested that the resonances arising from the 1,3 and 2,4 terminal positions were initially growing at equal rates and not at the 1:2 rate predicted by nonpreferential scrambling. This tentatively indicated that the 2,4 equatorial (e) and axial (a) positions were exchanging at different rates, which was not surprising since previous exchange studies of B_2D_6 and B_6H_{12} have established that protons on $-BH_2$ groups may be chemically nonequivalent. Unfortunately, the small chemical shift difference and the large line widths made it impossible to distinguish between 2,4e and 2,4a positions in the deuterium nmr.

Previous studies[11] have demonstrated that equatorial and axial resonances are resolved in the 220 MHz pmr of tetraborane(10). Examination of the spectra of μ-B_4H_9D *vs.* time (Figure 3) gave further proof that

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[9] STEPIT is a Fortran subroutine for finding local minima of almost any real function of several variables. It was written by J. P. Chandler, Indiana University, Physics Department and is available from the Quantum Chemistry Program Exchange, Department of Chemistry, Indiana University, Bloomington, Ind. 47401.

[10] A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," New York, N. Y., 1961, p 186.

[11] J. B. Leach, T. Onak, J. Spielman, R. R. Reitz, R. Schaeffer, and L. G. Sneddon, *Inorg. Chem.*, **9**, 2170 (1970).

the 2,4e and 2,4a positions were exchanging at different rates. Initially, the quartets arising from the 2,4e and 2,4a protons were present in equal intensity, but after deuterium scrambling was allowed to take place for 6 and 26 min at 22.5° (Figures 3b and c, respectively), the low-field quartet (the peaks indicated by X's in Figure 3) of the BH_2 set became diminished indicating that deuterium was entering this position. The high-field quartet of the BH_2 set appeared unaffected at these initial times, but after longer reaction times (Figure 3d), the two BH_2 quartets again appeared to be equal in intensity indicating that deuterium had equilibrated throughout the molecule.

For final proof of the above observations, the compound, μ-B_4D_9H was synthesized and its scrambling reaction *vs.* time monitored by 220 MHz pmr. The spectra in Figure 4 confirmed that the 1,3 and one 2,4 terminal position increase initially and that only upon longer reaction times does the other 2,4 terminal position exchange.

Several possible mechanisms for intramolecular exchange which fit the above qualitative information were suggested. (I) Two parallel first-order equilibrium reactions in which deuterium scrambles into the terminal positions by two different mechanisms

$$\begin{tikzcd}
 & \text{1,3 and 2,4 (e and a)} \\
\text{bridge} \arrow[ur, leftrightarrows, "K_1"] \arrow[dr, leftrightarrows, "K_2"'] & \\
 & \text{2,4 (e or a)}
\end{tikzcd}$$

(II) Two consecutive first-order equilibrium reactions in which deuterium scrambles first into the 1,3 and one 2,4 position before it can scramble into the other 2,4 position.

$$\text{bridge} \underset{\text{fast}}{\overset{K_1}{\rightleftharpoons}} \text{1,3 and 2,4 (e or a)} \underset{\text{slow}}{\overset{K_2}{\rightleftharpoons}} \text{2,4 (e or a)}$$

(III) A combination of I and II involving consecutive and parallel equilibrium reactions.

$$\begin{tikzcd}
 & \text{1,3} & \\
\text{bridge} \arrow[ur, leftrightarrows, "K_1"] \arrow[r, leftrightarrows, "K_2"'] & \text{2,4 (e or a)} \arrow[r, leftrightarrows, "K_3"] & \text{2,4 (e or a)}
\end{tikzcd}$$

In all cases we have assumed that equilibration of 1,3 to 2,4e and 2,4a by any direct process is negligible and the effective rate constant is $K_n = (k_n + k_{-n})$ where $k_n = k_{-n}$.

These models were tested by computer curve fitting of the experimental curves similar to those in Figure 1. A satisfactory fit of the data could be obtained for only mechanism I above. The values of the rate constants at various temperatures based on mechanism I are given in Table I.

If an initial rate method is used and the data treated as a simple first-order equilibrium between bridge and four terminal positions, a value for the effective rate constant is obtained which is in good agreement with the first rate constant obtained from mechanism I above. These values are also presented in Table I.

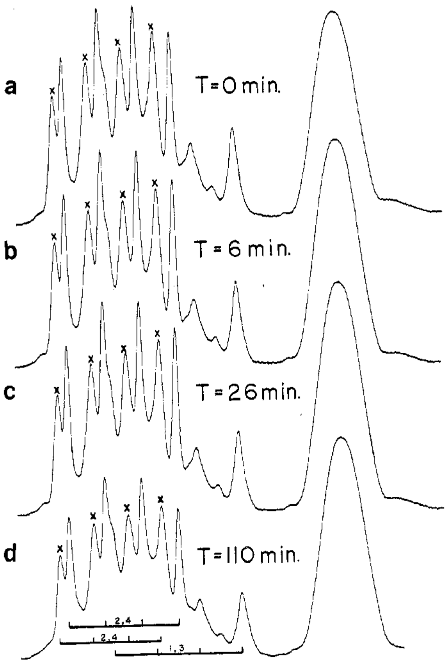

Figure 3.—Pmr (220 MHz) of μ-B_4H_9D scrambling reaction.

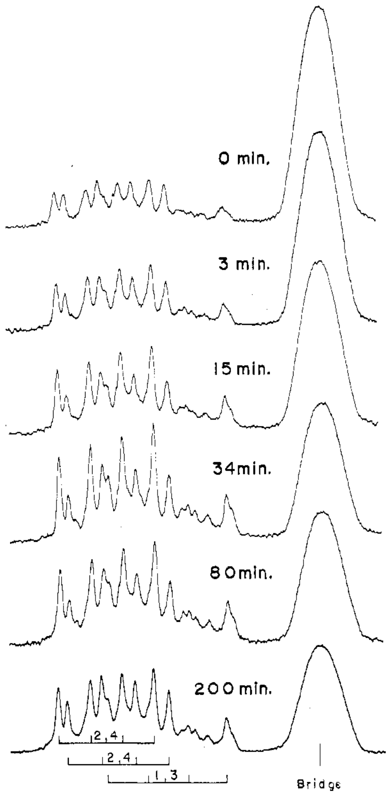

Figure 4.—Pmr (220 MHz) of μ-B_4D_9H scrambling reaction.

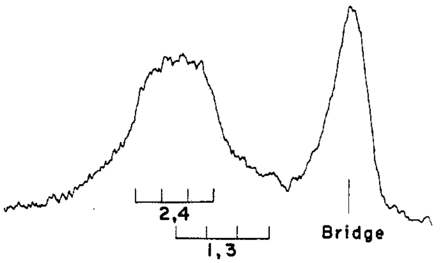

Figure 5.—Dmr (33.8 MHz) of B_2D_6–B_4H_{10} exchange reaction (30 min at 45°).

TABLE I

RATE CONSTANTS[a] FOR μ-B_4H_9D SCRAMBLING REACTIONS

Temp, °C	K_1, min$^{-1\ b}$	K_1, min$^{-1\ c}$	K_2, min$^{-1\ c}$
22.5	0.104 (4)	0.096 (4)	0.0031 (4)
19.0	0.050 (2)	0.050	0.0014
	0.051 (7)	0.050	0.0025
	0.043 (11)	0.041	0.0019
11.9	0.021 (2)	0.022	0.00071
	0.022 (2)	0.025	0.00075
5.5	0.0095 (6)		

[a] The effective rate constant, $K_n = k_n + k_{-n}$. [b] Rate constant obtained by neglecting the effect of the second rate. Standard errors are given in parentheses. [c] Rate constants were obtained by curve fitting. Errors are estimated on the basis of the deviation of the values at 19°.

TABLE II

ACTIVATION ENERGIES BASED ON DATA IN TABLE I

	ΔE_{act},[a] kcal	ΔE_{act},[b] kcal
K_1	18.5 (4)	18.5 (17)
K_2		21.5 (18)

[a] Value obtained when K_1 was determined by neglecting the effect of K_2. [b] Values obtained when K_1 and K_2 were determined by curve fitting of all data.

The activation energies given in Table II were obtained by an Arrhenius plot of the data in Table I.

The spectrum given in Figure 5 is typical of those obtained in the B_2D_6–B_4H_{10} gas-phase exchange reactions. In all cases, the 33.8 MHz deuterium spectra showed negligible concentrations of deuterium in the 1,3 terminal positions. In all cases, deuterium was found to be present in both bridge and the 2,4 terminal positions, the majority being in the 2,4 positions.

The B_2D_6–B_4H_{10} liquid-phase exchange reactions resulted in negligible deuterium exchange.

Discussion

The nature of the experiments yielding rate data must at best be considered crude. The error involved in spectral reproducibility as well as evaluation of the integrals precludes any firm conclusions based only on the values of the rate constants. For this reason, the activation energies must be regarded as only approximations.

Several important conclusions, however, can be drawn. Both qualitative and quantitative evidence presented above establishes that intramolecular hydrogen exchange in tetraborane(10) proceeds by two different rates. The faster rate involves the bridge and four terminal positions while the slower involves the bridge and the remaining two terminal positions.

On the basis of our kinetic results it would be foolhardy to propose any firm mechanism for intramolecular hydrogen exchange; however, one mechanism which equilibrates bridge to terminal (1,3 and 2,4e or a) positions and leaves the other 2,4 position unaffected may be visualized as a boron rotation mechanism with the requirement that rotation about the 2,4 boron atom can occur readily in only one direction as in Figure 6A or B.

Failure to fit model II or III above indicates that the rate for deuterium equilibration to the second 2,4 position is independent of deuterium scrambling to other terminal positions, so it is possible that scrambling to this last 2,4 terminal position is accomplished by a second, slower rotation approximately perpendicular to the first rotation (Figure 6A or B). These rotational motions in the molecule seem reasonable since they are consistent with a combination of the predicted vibrational modes in tetraborane(10).[12]

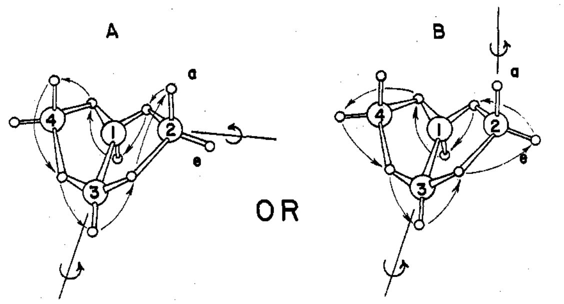

Figure 6.—Possible mechanisms for exchange in tetraborane(10).

Another possibility for deuterium migration to the last 2,4 terminal positions is that the rate depends upon the rate of intramolecular boron exchange. To test this possibility, rate data were obtained for the scrambling reaction of 4-$^{11}B^{10}B_3H_{10}$ by monitoring its 70.6 MHz ^{11}B nmr spectrum *vs.* time. The results were very crude, probably due to the large line widths and saturation effects, but a value of 5.7×10^{-4} min^{-1} was obtained for the scrambling of ^{11}B from the 4 position to the 1,3 position. This gives a value of $1.14 \times 10^{-3} \pm 1.0 \times 10^{-4}$ for the rate of 2,4 to 1,3 interconversion in tetraborane(10) at 19°. Referral to Table I indicates that K_2 for the exchange of deuterium in B_4H_9D is approximately the same and may be dependent on the rate of intramolecular boron exchange. However, any conclusions drawn from these data must be considered tentative since the sensitivity of measurement for the data on which these two rate constants are based is very low.

Previous studies of the B_2D_6–B_4H_{10} gas-phase deuterium exchange reaction had demonstrated that two hydrogen positions in tetraborane(10) exchange at a faster rate than the other hydrogens in the molecule. It was suggested that the faster rate led to the formation of 1,3-$B_4H_8D_2$. This suggestion is inconsistent with our present findings since we have shown that the 1,3 terminal positions are involved in a rapid intramolecular exchange with the bridges and one 2,4 terminal position. However, it seemed reasonable that a 2,4-$B_4H_8D_2$ labeled compound could be formed (labeled in the 2,4 position not involved in the rapid intramolecular exchange) and we duplicated the original experiments to investigate this possibility. We found no evidence for the formation of a 1,3-$B_4H_8D_2$. All deuterium spectra of the gas-phase reactions indicated large concentrations of deuterium in the 2,4 terminal and bridge positions and negligible amounts in the 1,3 positions.

Although these results appear to exclude the formation of 1,3-$B_4H_8D_2$ in the B_4H_{10}–B_2D_6 exchange reaction it is still possible that a 2,4-$B_4H_8D_2$ is formed initially, but all attempts to prepare this compound were unsuccessful.

Acknowledgment.—Support of this work by the National Science Foundation through grants GP-4944X and GP-24266X is gratefully appreciated. We also wish to thank Mr. R. F. Childers and Mr. and Mrs. J. C. Huffman for many helpful discussions.

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(12) A. J. Dahl, Ph.D. Thesis, University of Michigan, Ann Arbor, Mich., 1963.