

was cleanly resolved into components at 2.94 and 3.0 microns, but the B-H band at 4.2 to 4.3 microns was broad. In diglyme the N-H doublet at 2.96 microns was not resolved but the B-H band was cleanly split into components at 4.18 and 4.32 microns with an unresolved shoulder at 4.1 microns. Some structure may also be observed in the 6.4 micron band. Split N-H and B-H frequencies suggest the presence of NH_2 and BH_2 groups in the molecule.

The ^{11}B n.m.r. spectrum of the compound in diglyme solution was obtained at 19.3 Mc/s. with a Varian DP-60 Spectrometer and was found to consist of a single symmetrical 1:2:1 triplet. Thus, direct evidence is at hand showing that all boron atoms in the molecule are equivalent within the sensitivity of the method and are attached to two hydrogens (hydrolytic analysis only demonstrated that six hydrolyzable hydrogens are present for a total of three boron atoms). Possibility of a linear structure with B-H and BH_3 groups is thus eliminated. A satisfactory proton n.m.r. spectrum was not obtained owing to the low solubility of the compound in non-hydrogen containing solvents.

F. Powder Pattern.—In Table I are recorded characteristic interplanar spacings (d values) for hexahydroborazole. The powder pattern was obtained with a Phillips Geiger Counter Spectrometer with the powder in a flat, open aluminum holder and using copper $K\alpha$ radiation. No evidence for change of the pattern with time was observed, although no protection from the atmosphere was provided.

TABLE I

d	l	d	l
2.576	m.	3.07	m.
2.583	m.	3.10	m.
2.72	m.	3.95	m.
2.84	s.	4.50	s.
3.00	m.	5.79	v.s.
		6.28	v.s.

Discussion

Probably the most striking feature observed thus far in the study of hexahydroborazole is its highly polar character as indicated both by solubilities and by its lack of volatility. This follows, of course, from the positive and negative charges which alternate in the ring, but the intermolecular forces are much larger than had been anticipated by us. It is interesting to speculate on the possibility that strong transannular attractions may serve to enhance the stability of the boat form relative to the chair form—possibly to a degree sufficient to

allow positional isomerism. A more detailed structural investigation has been initiated with this in mind. It is probable that study of hexahydroborazole and its derivatives can add substantially to our knowledge of conformational characteristics of organic compounds by providing models with the most extreme polar character.

It should be noted that four different groups of investigators have reported preparation of a polymeric form of BH_2NH_2 .⁹⁻¹² The possibility of obtaining hexahydroborazole from the polymeric material deserves further attention.

Despite the somewhat unsatisfactory molecular weight measurements, the empirical formula, spectral information and decomposition studies can leave little doubt that the six membered ring structure has in fact been retained.

It is worth observing that if donation of an electron pair from nitrogen to boron were complete in borazole itself, the resulting charge distribution would be closely similar to that in hexahydroborazole and intermolecular attractions might be expected to be of comparable magnitude. In fact, borazoles are more volatile than the aromatic hydrocarbons. Thus, comparison of physical properties suggests that only relatively slight contribution of double bonded structures is present in borazole (and hence only relatively little resonance stabilization) in agreement with the more recent theoretical calculations.¹³

Acknowledgment.—Support of this research by NSF Grant 6224 and by a subcontract with the U. S. Borax Research Corporation under Air Force Contract AF 33(616)-7303 is gratefully acknowledged.

(9) E. Wiberg and P. Buchheit, *Z. anorg. Chem.*, **256**, 285 (1948).

(10) H. I. Schlesinger, D. M. Ritter and A. B. Burg, *J. Am. Chem. Soc.*, **60**, 2297 (1938).

(11) G. W. Schaeffer and L. J. Basile, *ibid.*, **77**, 331 (1955).

(12) H. C. Hornig, W. L. Jolly and G. W. Schaeffer, Abstracts of Papers Presented at the 131st American Chemical Society Meeting, Miami, Florida, April, 1957, page 4-R.

(13) For a discussion of recent work see H. Watanabe, K. Ito and M. Kubo, *ibid.*, **82**, 3294 (1960).

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Studies of Boron-Nitrogen Compounds. IV. Isotopic Exchange Reactions of Borazole

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The exchange of hydrogen between borazole and various compounds containing deuterium has been studied. Isotopic exchange was followed with a mass spectrometer and position of substitution characterized by infrared spectra. Deuteriated ammonia, deuterium chloride and deuterium cyanide exchange with the hydrogen attached to nitrogen atoms in the borazole ring at a rate comparable to that with which they add. The addition of hydrogen cyanide was found to be largely reversible. Molecular deuterium, diborane- d_6 and sodium borodeuteride undergo exchange with the hydrogens attached to boron atoms in the borazole ring. Borazole reacted rapidly with deuteriated ethanol and deuterium oxide but no isotopically substituted borazole was present in the recovered material. Neither exchange nor chemical reaction occurred with deuterium sulfide, deuteriated acetylene nor deuteriated phosphine. A partial mass spectrometric investigation of the borazole molecule and isotopic derivatives shows that the $\text{B}_3\text{N}_3\text{H}_5^+$ fragment (the most abundant ion in the mass spectrum) is primarily formed by loss of a hydrogen from a boron atom.

Borazole, $\text{B}_3\text{N}_3\text{H}_6$ possesses a six-membered ring structure of alternate boron and nitrogen atoms.

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The physical constants of this substance and its derivatives are remarkably similar to those of benzene and corresponding derivatives with which they are isosteric and isoelectronic. The older literature abounds in comparisons of borazole

compounds with their respective benzene analogs; yet the dissimilarity of the atoms and the molecule and the polarity of the bonds results in a chemical behavior substantially different from that of aromatic hydrocarbons.

Study of the isotopic exchange reactions of borazole was felt to be desirable both for a better understanding of its chemical behavior as well as to provide methods for preparation of the various selectively deuterated derivatives for future use in kinetic studies and tracer investigations.

Experimental

The apparatus and methods employed in the purification, isolation and identification of volatile products have been adequately described by Sanderson.² All pressures are given in millimeters of mercury and all gas volumes, unless otherwise stated, are given in cubic centimeters of gas at zero degrees and 760 mm. pressure. Borazole was prepared by the method of Dahl and Schaeffer³ and was purified further by high vacuum fractionation before use.

Infrared spectra were obtained with a Perkin-Elmer Infracord Spectrometer Model No. 137 in a gas cell of 100 cc. volume. Mass spectra were obtained with a Consolidated Engineering Mass Spectrometer Model No. 21-620. Since mass spectra of various borazoles have been studied recently in some detail by Loughran, *et al.*,⁴ no extensive investigation of the mass spectra of deuterium substituted borazoles was undertaken. In general, only mass peaks above a m/e ratio of 74 were recorded to identify and detect isotopic exchange. Samples were run at pressures of 75 to 100 microns using an ionizing current of 20 milliamperes.

Deuterium oxide and deuterium gas were obtained from the Stuart Oxygen Company of San Francisco and were claimed to be of greater than 99.5% purity. Deuterated ammonia was prepared by treatment of magnesium nitride with deuterium oxide followed by high vacuum purification. Decomposition of a sample on a hot platinum wire followed by measurement of the hydrogen-deuterium ratio mass spectrometrically showed the sample to be of greater than 96% isotopic purity. Deuterated acetylene, deuterated phosphine, deuterium chloride, deuterium cyanide and deuterium sulfide were prepared by hydrolysis of suitable salts with deuterium oxide. Deuterated ethanol was kindly supplied by Professor V. J. Shiner, Jr., and had earlier been shown by him to be 98% deuterated in the hydroxyl group. Deuterated diborane was supplied through the courtesy of Professor H. I. Schlesinger of the University of Chicago. Deuterated sodium borohydride was prepared by the method of W. G. Brown, *et al.*, and had a deuterium content of about 50%.⁵

Exchange of Borazole with Deuterium.—At temperatures above 100° borazole exchanged at a convenient rate with deuterium gas. This exchange could be conveniently followed by observing the gradual growth of peaks at 82, 83, and 84 mass numbers as the reaction continued. Even at relatively long heating periods no peaks above 84 appeared in the mass spectrum providing conclusive proof that only three hydrogen atoms on the borazole ring were involved in the exchange reaction.

In a typical reaction a clean 50 ml. bulb with attached stopcock was filled with about 60 mm. of borazole, the borazole condensed at -196° and deuterium admitted to a pressure of 113 mm. The bulb was heated for 75 minutes at 195°, the hydrogen-deuterium mixture removed and a small portion of the borazole introduced into the mass spectrometer. Peaks at 81, 82, 83 and 84 had relative intensities of 85, 100, 41 and 31.6. The borazole was again condensed with liquid nitrogen and an additional 82 mm. pressure of deuterium introduced into the bulb and the bulb heated for 70 minutes at 195°. The 81 to 84 mass

spectral peaks now showed intensities of 71, 100, 34.5 and 39, respectively. The borazole was again condensed, 64 mm. of deuterium introduced and the sample heated for 60 minutes at 195°. The mass spectral values for the top four peaks were now 68, 100, 35.8 and 42.7. In a fourth exchange, 71 mm. of deuterium was admitted and the sample heated 1 hr. at 195°. Following the fourth exchange the relative intensities were 69.6, 100, 34.8 and 42.2, respectively, substantially unchanged from the starting material. The infrared spectrum of this sample was determined and showed essentially complete elimination of the B-H stretching frequency at about 3.8 microns and complete retention of the N-H stretching frequency at 2.8 microns. However, a new intense band at 5.3 microns had appeared corresponding to the B-D stretching frequency.

Several attempts were made to follow quantitatively the rate of exchange of deuterium with borazole at 127.5°. However, despite all efforts to use reproducible experimental conditions, no reliable values for rates of reaction could be obtained. In one experiment two flasks of equal volume containing equal quantities of borazole and deuterium were carried through exchange reactions simultaneously. One flask was filled with Pyrex glass wool. Reproducible rate curves were not obtained from either reaction but it appeared that in all runs the reaction progressed more slowly in the reaction vessel filled with glass wool.

An attempt to initiate the isotope exchange between borazole and deuterium at room temperature with methyl radicals formed by the photochemical decomposition of azomethane was not successful.

Reaction between Borazole and Diborane- d_6 .—In a typical reaction 0.2 mmole of diborane- d_6 and 0.11 mmole of borazole were introduced into a glass vessel, sealed from the vacuum system and allowed to remain at room temperature for thirty minutes. The reactants were again introduced into the vacuum system and separated by fractional distillation through a -95° trap. A mass spectrum of the recovered borazole showed peaks up to $m/e = 84$ indicating that exchange of only three of the six hydrogens in the borazole molecule had occurred. The infrared spectrum showed the characteristic appearance of a B-D band at 5.3 microns and the substantial decrease in intensity of the B-H band at about 3.8 microns. Clearly, selective exchange of the three hydrogens attached to boron atoms in the borazole molecule had occurred.

Exchange of Borazole with Sodium Borodeuteride.—The exchange of borazole with partially deuterated sodium borohydride was studied under several conditions.

About 2.0 mmoles of partially deuterated sodium borohydride were introduced into a flask of 5 cc. volume under a stream of dry nitrogen and 0.31 mmole of borazole added. The reaction flask was allowed to remain for 5 hr. at room temperature with a liquid phase of borazole present. On opening and subjecting the recovered borazole to mass spectral analysis no peaks of m/e greater than 81 could be observed. Hence, no exchange had taken place under these conditions. In a new experiment, about 2.0 mmoles of partially deuterated sodium borohydride was dissolved in 1 ml. of diglyme and 0.31 mmole of borazole added. After the mixture had been allowed to remain at room temperature for several hours, about one-sixth of the borazole was recovered by fractional distillation but the mass spectrum indicated that substantially no deuterium exchange had occurred during this time. The relative intensity of the peak at 82 mass units was only 1.2% and no higher masses were observed.

In a third experiment, about 0.18 mmole of borazole was heated with 2.0 mmoles of partially deuterated sodium borohydride for 3 hr. at 150°. When the bulb was opened, no noncondensable gas was found to be present but the mass spectrum of the borazole showed peaks up to $m/e = 84$ and the infrared spectrum clearly showed the new B-D band at 5.3 microns indicating that exchange of the hydrogens attached to borons in the borazole molecule had taken place.

Exchange of Borazole with Deuterated Ammonia and N-Deuterated Diethylamine.—The reaction of borazole with many compounds of the general type HX is known to be rapid and to lead to nonvolatile products.⁶ In particular, such addition occurs rapidly with protons attached to halogens, nitrogen or oxygen. Nevertheless, it was felt that

(2) R. T. Sanderson, "High Vacuum Manipulation of Volatile Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948.

(3) G. Dahl and R. Schaeffer, *J. Inorg. Nuclear Chem.*, **12**, 380 (1960).

(4) E. D. Loughran, C. L. Mader and W. E. McQuiston, U. S. Atomic Energy Commission Report LA-2368, Los Alamos Scientific Laboratory, January 14, 1960.

(5) W. G. Brown, L. Kaplann and K. E. Wilzbach, *J. Am. Chem. Soc.*, **74**, 1343 (1952).

(6) See many papers and reviews by E. Wiberg; for example, E. Wiberg, *Naturwissenschaften*, **35**, 182, 212 (1948).

at sufficiently low temperatures some recovery of borazole might be achieved and permit some conclusions concerning isotopic exchange.

In a typical reaction, 0.73 mmole of deuteriated ammonia was mixed with 0.23 mmole of borazole in a flask of 3 cc. volume and the mixture allowed to remain at -50° for about five minutes. Rapid fractionation through a -95° trap retained some borazole and by subsequent fractionation 0.12 mmole of borazole and 0.56 mmole of ammonia were recovered. The mass spectrum of the recovered borazole showed a highest mass of 84 indicating that only three hydrogen atoms in the borazole molecule had exchanged. The infrared spectrum of the partially exchanged sample showed decreased intensity of the characteristic N-H band at 2.8 microns and the appearance of a new N-D band at 3.8 microns partially superimposed on the B-H band.

It was of interest in connection with the mechanism to determine whether exchange between borazole and ammonia would occur in the gas phase as well as in liquid phase at low temperature. A reaction vessel was constructed from two 50 ml. bulbs connected by a 4 mm. vacuum stopcock. The reactants were placed in the separate bulbs, 0.13 mmole of borazole in one and 0.48 mmole of deuteriated ammonia in the other and the individual samples allowed to reach room temperature. The stopcock between the bulbs was then opened and the ammonia allowed to expand into the bulb containing the borazole. After remaining at room temperature for 25 minutes small amounts of a white solid had been deposited on the walls of the flask. A mass spectrum of the recovered borazole showed that no exchange had taken place.

The exchange reaction between borazole and N-H bonds in amines is probably of fair generality. Only one other exchange reaction was investigated in this work, however. N-Deuteriated diethylamine was prepared by exchange with water and 0.41 mmole of it allowed to react with 0.12 mmole of borazole at -30° for three minutes. Separation of the reactants proved difficult by conventional fractional condensation techniques, but a mass spectrum of the total mixture was taken since the peaks of interest in the borazole molecule fall above the highest peaks in the diethylamine spectrum. It was clear that three hydrogens in the borazole molecule had undergone exchange, but in absence of separation from residual diethylamine it could not be confirmed by infrared spectra that exchange had actually occurred at the protons attached to the nitrogen atoms in borazole.

Exchange of Borazole with Deuterium Chloride.—The reaction of borazole with hydrogen chloride occurs rapidly but it appeared of interest to study the possibly competitive exchange reaction. Consequently, 0.14 mmole of borazole and 0.63 mmole of deuterium chloride were condensed into a 5 cc. reaction flask and allowed to warm to room temperature for 15 minutes. Formation of solid occurred but on fractional condensation of the volatile materials through a -90° trap some borazole was recovered. The mass spectrum of the borazole showed peaks only up to $m/e = 84$ indicating that only three hydrogen atoms of the borazole molecule had undergone exchange. An infrared spectrum of the recovered borazole showed decreased intensity of the N-H band and appearance of the N-D band. In a separate experiment 0.64 mmole of deuterium chloride and 0.17 mmole of borazole were mixed in the gaseous phase at room temperature in the reaction flask used earlier for the gas phase reaction between deuteriated ammonia and borazole. The reaction mixture was allowed to stand for 10 minutes and during this time a non-volatile white precipitate formed on the walls of the reaction vessel. Fractionation of the volatile contents recovered 0.25 mmole of deuterium chloride and 0.03 mmole of borazole (indicating nearly the expected ratio in the solid product). The mass spectrum of the recovered borazole again indicated that exchange had taken place between borazole and deuterium chloride in the gas phase.

To check the possibility that partially deuteriated borazole had resulted from an exchange with the nonvolatile solid formed during the reaction, 0.02 mmole of borazole was allowed to stand for 3 hr. at room temperature over 0.19 mmole of the deuterium chloride adduct of borazole which had been deposited on the walls of a reaction flask of 50 ml. volume. All of the borazole was recovered and the mass spectrum showed that no measurable hydrogen-deuterium exchange had taken place.

Finally, 0.18 mmole of the deuterium chloride adduct of

borazole was heated with 1.49 mmole of triethylamine at 85° for 7 hr. After this time 0.04 mmole of noncondensable gas, presumably hydrogen, had been formed but 0.05 mmole of borazole could be recovered by fractional condensation. Mass spectrum of the recovered borazole showed that exchange had indeed occurred but the sample recovered was too small to allow conclusive proof that the borazole was N-deuteriated.

Exchange of Borazole with Deuterium Cyanide.—A mixture of 0.51 mmole of borazole and 2.07 mmoles of deuterium cyanide was allowed to stand at room temperature for 1 hr. During this time no visible reaction had occurred and no isotope exchange had taken place as shown by a mass spectrum of the gas mixture. However, when the reaction flask was briefly chilled to obtain a liquid phase a white precipitate formed immediately. Some unreacted borazole was still present after the flask had warmed to room temperature again and its mass spectrum revealed that a partial exchange of hydrogen by deuterium had taken place.

Since the reaction of borazole with hydrogen cyanide has not been studied previously, a more comprehensive investigation of this reaction was undertaken. The observation that reaction does not occur in the gas phase was again confirmed but by repeated chilling to produce a liquid phase, reaction was produced between a mixture of 0.52 mmole of borazole and 3.85 mmole of hydrogen cyanide. When repeated cooling produced no more precipitate, 2.20 mmoles of hydrogen cyanide were recovered showing that 1.65 mmoles of hydrogen cyanide had been consumed by 0.52 mmole of borazole. Thus the over-all reaction, as in the case of many other HX compounds, corresponds reasonably well to the formation of an adduct of formula $B_2N_2H_4 \cdot 3HCN$.

The hydrogen cyanide adduct of borazole was soluble in diglyme but insoluble in carbon tetrachloride and chloroform. It appeared stable on heating to 115° for several hours since it neither changed in physical appearance nor formed volatile materials. A sample of 87.5 mg. of the adduct was heated to 162° until the evolution of volatile materials ceased. After 2 hr. 0.14 mmole of noncondensable gas had been formed. Assuming that as in the case of decomposition of other HX adducts three molecules of hydrogen are eliminated, only 10% of the hydrogen cyanide adduct had decomposed in this fashion. After separation of the hydrogen the remaining volatile material was transferred to an infrared cell and shown to be a mixture of hydrogen cyanide and borazole. Re-formation of the adduct prevented a quantitative determination of the amounts of borazole and hydrogen cyanide which had been formed. However, a rough estimate of the volume of the decomposition products showed that 3.3 mmoles of volatile materials had been produced per mmole of adduct used (taking no account of adduct which lost hydrogen). Since one mole of the adduct produces four moles of gaseous condensable products if it dissociates to the original reactants, it appears that the primary thermal decomposition of the hydrogen cyanide adduct of borazole produces the original reactants.

Studies in which Borazole Exchange Reactions were not Observed.—To attempt to obtain further information about the nature of the exchange process, studies of possible exchange of borazole with a number of other deuteriated compounds were made. Since lack of exchange is equally significant chemical information, a brief report of these experiments seems desirable. Borazole did not exchange with phosphine- d_3 in the liquid phase at -80° during a 2 hr. period, at -50° in a five minute period, at room temperature in a 26 hr. period, nor at 135° during a 1 hr. period. Neither exchange with phosphine nor reaction occurred under any of these conditions.

No exchange or reaction occurred with deuterium sulfide at -30° in five minutes with a liquid borazole phase present, in the gas phase at room temperature in 12 hr., nor in the gas phase at 103° in 55 minutes. Quantitative recovery of the reactants could be accomplished in each experiment.

After borazole had been treated with deuterium oxide for 15 minutes at 0° , one-third of the borazole could be recovered but had not undergone exchange. In a separate experiment phosphorus pentoxide was added to the water to test the possibility that acid catalysis might be effective but again no exchange could be observed in the recovered borazole. When trimethylamine was added to search for a

possible base catalyzed exchange, hydrolysis of the borazole was so extensive that no recovery could be made.

After reaction with deuterated ethanol at -45° for five minutes, recovered borazole showed that no exchange had taken place.

Borazole neither reacted with nor exchanged with acetylene-*d*₂ in the liquid phase at -50° in 10 minutes, in the gas phase at room temperature in 5 minutes, nor in the gas phase at 80° in 30 minutes.

Discussion

Clearly at least two mechanisms are operative in the isotope exchange reactions of borazole since exchange occurs so selectively either on the boron or nitrogen atoms. Any detailed discussion of possible mechanisms would not be warranted on the basis of presently available information. Perhaps the most significant and singular conclusion that can be drawn concerning exchange mechanisms arises from the deuterium chloride studies. Thus it has been established that the adduct B₃N₃H₆·3HCl does not decompose to borazole under the conditions of the exchange nor does it exchange with borazole once formed. Since exchange occurs when borazole and deuterium chloride are mixed, at least one reversible step must be involved before the final removal of material as the nonvolatile, unreactive adduct. Thus, it may well be that reaction takes place by electrophilic attack at the nitrogen atom followed by transfer of chloride to the boron to complete addition or abstraction of the adjacent hydrogen attached to nitrogen by the chloride ion resulting in exchange.

Relatively pure samples of B₃D₃N₃H₃, B₃H₃N₃D₃ and B₃D₃N₃D₃ have been prepared. The perdeuterio compound is most readily prepared by reaction of diborane-*d*₆ with ammonia-*d*₃. The B-deuterated compound is most readily prepared by exchange of borazole directly with deuterium as reported above. The N-deuterated compound is most readily prepared from the perdeuterio compound by back exchange with hydrogen to remove the deuterium attached to boron. Unfortunately, a mass spectrometrically pure N-deuterated borazole was not obtained in this fashion.

Comparison of the three heaviest ions formed by electron bombardment of B₃H₃N₃H₃, B₃D₃N₃H₃, B₃H₃N₃D₃ and B₃D₃N₃D₃ (81, 80, 79; 84, 83, 82; 84, 83, 82; and 87, 86, 85, respectively) provides interesting qualitative information. The necessary data are given in Table I. Both of the N-

TABLE I
PARTIAL MASS SPECTRA OF ISOTOPIC BORAZOLES

	<i>(Relative intensities)</i>		
	<i>M</i> ^a	<i>M</i> ^a - 1	<i>M</i> ^a - 2
B ₃ H ₃ N ₃ H ₃	34.3	100.0	63.1
B ₃ D ₃ N ₃ H ₃	41.2	34.8	100.0
B ₃ H ₃ N ₃ D ₃	28.9	87.8	100.0
B ₃ D ₃ N ₃ D ₃	39.2	35.8	100.0

^a *M* is the highest isotopic peak in each case (81, 84 or 87).

deuterated materials were known to be somewhat contaminated with N-H derivatives. Nevertheless, it is qualitatively apparent that when hydrogen is attached to boron the intensities of ions with mass one less than the parent ion are greater than when deuterium is bonded to boron. In the case of B₃D₃N₃H₃ a partial analysis of the spectrum (using a ¹⁰B/¹¹B ratio of ²⁰/₈₀) shows that an ion of composition B₃D₃N₃H₂⁺ is only 9.6% of the parent peak. If a similar ratio may be applied to B₃N₃H₆ itself, one can calculate that about 95% of the first ionization of hydrogen is accounted for by loss of hydrogen from boron. No allowance for an isotope effect has been made. It would be valuable to compare the above calculation with one based on B₃H₃N₃D₃, but no sample of sufficient isotopic purity has been prepared in these Laboratories. It is interesting to observe that the conclusion reached above is in agreement with the interpretation of Loughran, *et al.*, based on the relatively low (11.5 volt) appearance potential for the B₃N₃H₅⁺ ion.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE JOHNS HOPKINS UNIVERSITY, BALTIMORE 18, MARYLAND]

The Isotopic-Exchange Reactions of B₂H₆ with DT, HT and HD

By J. S. RIGDEN AND W. S. KOSKI

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The isotope effects of the diborane-hydrogen exchange and in the pentaborane-diborane exchange reactions have been studied using deuterium and tritium as tracers. In the former reaction an inverse isotope effect was observed, whereas in the latter a normal isotope effect was obtained. The effects are interpreted in terms of previously proposed mechanisms.

Introduction

A number of exchange reactions involving boron hydrides have been studied; however, in none of these studies has the isotope effect been investigated. In view of the fact that a large isotope effect may influence mechanistic conclusions drawn from exchange data, it was decided to investigate the difference in exchange rates of deuterium and tritium in boron hydrides. The reaction selected for this initial study was the hydrogen-diborane exchange. This reaction was first studied by

Maybury and Koski¹ using deuterium as a tracer. It was found that the reaction was 3/2-order with respect to diborane and the deuterium order was dependent upon the initial deuterium concentration. At low initial deuterium concentrations the reaction was first order with respect to deuterium while at high initial concentrations it had a zero order dependence on deuterium. The reaction also showed a weak but definitely measurable surface dependence.

(1) P. C. Maybury and W. S. Koski, *J. Chem. Phys.*, **21**, 742 (1953).