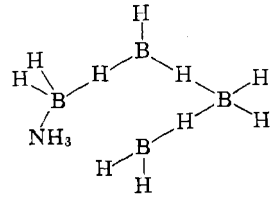


Parry and Shore[16] have discussed the possibility of a diborane analog of this molecule, and other studies have indicated that base displacement of a bridge hydrogen can occur before cleavage takes place in reactions of diborane with trimethylamine[17] and with ethers.[18]

In addition to yielding mechanistic information about the reaction of tetraborane with tetrahydrofuran, the formation of $(C_4H_8O)_2BH_2^+$ provides a reactive boron hydride cation which may have synthetic utility.

Acknowledgment.—This work was supported by the National Science Foundation under Grant NSF-G-14595.

---

(16) R. W. Parry and S. G. Shore, *J. Am. Chem. Soc.*, **80**, 15 (1958).

(17) S. H. Bauer and J. V. Martinez, paper presented at the International Symposium on Boron–Nitrogen Chemistry, Duke University, Durham, N. C., April 23–25, 1963, p. 338.

(18) D. F. Gaines, *Inorg. Chem.*, **2**, 523 (1963).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE
UNIVERSITY OF MICHIGAN, ANN ARBOR, MICHIGAN

A Tracer Study of the Reaction between Tetraborane and Sodium Tetradeuterioborate(III)

BY R. W. PARRY, R. W. RUDOLPH, AND D. F. SHRIVER

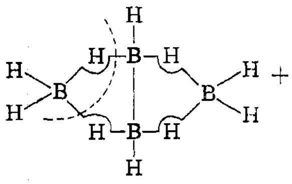
Received May 25, 1964

Tetraborane (B_4H_{10}) and sodium tetradeuterioborate(III) ($NaBD_4$) were allowed to react in ethylene glycol dimethyl ether at −45°. The resulting diborane and sodium triborohydride (NaB_3H_8) were analyzed for deuterium. The data clearly indicate that under the conditions used in this study a BH_3 group is split from the tetraborane and a deuteride ion is transferred from the BD_4^- to the resulting B_3H_7 to give as final products NaB_3H_7D and a mixture of diborane molecules whose over-all composition is consistent with the formula $B_2H_3D_3$.

It has been convenient to describe much of the chemistry of diborane and tetraborane in terms of symmetrical and nonsymmetrical cleavage of the double hydrogen bridge bonds.[1,2] Symmetrical cleavage of B_4H_{10} gives products which may be formally derived from BH_3 and B_3H_7 fragments while nonsymmetrical cleavage gives products derived from H_2B^+ and $B_3H_8^-$. While identification of reaction products usually provides a firm basis for reaction classification, it does not provide definite evidence about reaction mechanism. Indeed, in several cases it has not even been possible to classify the cleavage process on the basis of product identification. For example, the reaction between B_4H_{10} and $NaBH_4$, first described by Hough and Edwards,[3] can be given by the equation

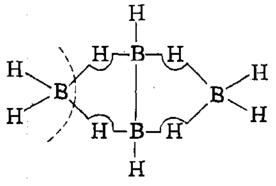
$$NaBH_4 + B_4H_{10} \longrightarrow NaB_3H_8 + B_2H_6$$

The NaB_3H_8 and B_2H_6 could arise from BH_3 and B_3H_7 fragments of tetraborane formed by symmetrical cleavage or from BH_2^+ and $B_3H_8^-$ fragments formed by nonsymmetrical cleavage. Direct information on the nature of the reaction process can be obtained from a tracer study using $NaBD_4$ and B_4H_{10} as indicated below.



$$+ NaBD_4 \longrightarrow NaB_3H_7D + B_2H_3D_3$$
12% D 50% D

symmetrical cleavage



$$+ NaBD_4 \longrightarrow NaB_3H_8 + B_2H_2D_4$$
0% D 67% D

unsymmetrical cleavage

The results of the study described herein indicate clearly that a symmetrical cleavage process is involved. The observations are also consistent with the boron labeling experiments of Schaeffer and Tebbe,[4] who synthesized tetraborane with a known boron isotope located in the 4-position. The B_4H_{10} synthesis involved the reaction of B^{10}-enriched NaB_3H_8 with HCl and normal B_2H_6. The boron position indicated addition of a boron to the three-boron cluster in the expected fashion but did not differentiate between possible addition of BH_3 to B_3H_7 or of BH_2^+ to $B_3H_8^-$. The tracer result on the reverse process described below

---

(1) R. W. Parry and L. J. Edwards, *J. Am. Chem. Soc.*, **81**, 3554 (1959).

(2) G. Kodama and R. W. Parry, *ibid.*, **81**, 3534 (1960); *ibid.*, **82**, 6250 (1960).

(3) W. V. Hough and L. J. Edwards, "Borax to Boranes," Advances in Chemistry Series, No. 32, American Chemical Society, Washington, D. C., 1961, p. 190.

(4) R. Schaeffer and F. Tebbe, *J. Am. Chem. Soc.*, **84**, 3974 (1962).

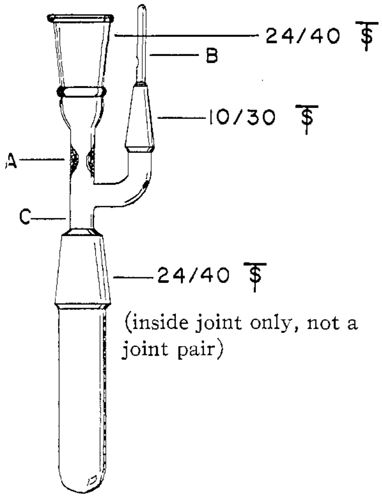


Fig. 1.—Reaction vessel.

would suggest the addition of the BH_3 group as in the first choice.

Experimental

(1) **Materials and Preparation of Vacuum System.**—All reactions and separations were carried out on a vacuum line under strictly anhydrous conditions. $NaBD_4$ was purified by filtering its liquid ammonia solution using a vacuum line filtration assembly.[5] Tetraborane was redistilled from a trap at −98° into a trap at −126° before use. Ethylene glycol dimethyl ether (Ansul 121), b.p. 83.2–83.7°, and diethyl ether were stored over NaH at 25° until no more H_2 was evolved (5 days) and were distilled directly from $LiAlH_4$ into the appropriate reaction vessel. Benzene was stored over NaH.

Protium contamination during handling of the partially deuterated products was minimized by preliminary conditioning of the vacuum equipment. D_2O was introduced into the vacuum line and removed. Diffusion pumps than maintained the pressure at less than 5×10^{-5} mm. for about 2 hr. Sufficient B_2D_6 to give a pressure of about 200 mm. was added to the system, allowed to stand for about 2 hr., and then removed. Finally, the glass walls were heated with a flame while the high vacuum pumps were operating.

(2) **The Reaction Procedure.**—The reaction vessel, shown in Fig. 1, was conditioned as noted above, dry N_2 was added to the system, a weighed quantity of $NaBD_4$ was carefully added, B_4H_{10} and the Ansul 121 polyether solvent were distilled into the tube, the contents of the tube were frozen with liquid N_2, and the evacuated reaction vessel was sealed off at point A. The *entire* reaction tube and side tube system was then immersed in a bath at a uniform temperature of −45°.[6]

The vessel and contents were held at −45° for time intervals as indicated in Table I. Diborane and some solvent were then distilled from the reaction vessel (−45°) through the break-off tip B into the vacuum system (−196°). Pure B_2H_6 was separated from the mixture by fractionation (−112 and −196°) and pyrolyzed at 700° in a Vycor tube containing chunks of uranium metal. The evolved H_2, D_2, and HD mixture was equilibrated over a hot tungsten filament and analyzed by the mass spectrometer.

The ether on the solid NaB_3H_8 in the reaction tube was removed at room temperature under high vacuum over a period of 1 week. The reaction tube was then broken off at point C and fastened to a vacuum line filtration assembly. Residual solids were washed from the NaB_3H_8 with dry benzene. Finally, NaB_3H_8 was separated from any excess $NaBD_4$ by dissolving the former in diethyl ether and filtering it directly into a Vycor pyrolysis tube which was used as the receiver for the vacuum filtration assembly.[7]

The receiver tube also contained chunks of uranium metal for use in later pyrolysis. The ether was distilled from the NaB_3H_8; then the pure solid was pyrolyzed at a temperature of 750° in the presence of uranium metal. The evolved hydrogen–deuterium mixture was equilibrated and analyzed as before. Results are shown in Table I.

(3) **Calibration of the Mass Spectrometer.**—The mass spectrometer was calibrated using standard, equilibrated mixtures of protium and deuterium. The mixtures were made from weighed amounts of H_2O and D_2O which were decomposed over granulated zinc at 400°, then equilibrated over a tungsten filament prior to analysis. In all analyses contact of the gas with stopcock grease was minimized.

(4) **The Decomposition of Tetraborane in Ethylene Glycol Dimethyl Ether (Ansul 121) at −45°.**—Tetraborane (0.996 mmole) was condensed in a reaction tube containing about 7 ml. of the polyether. The tube was sealed off under vacuum and held at −45° for 62.5 hr. The vessel was then opened to the vacuum system; volatiles were pumped from the reaction tube (−45°) through a trap at −95° and into a trap at −196°. The −196° fraction was identified as B_2H_6 (0.477 mm.) by its infrared spectrum.

Care was taken to avoid contact between B_4H_{10} and polyether above −45°, hence the conditions are the same as those which prevailed during the B_4H_{10}–$NaBD_4$ reaction. Under these conditions data are consistent with the equation

$$B_4H_{10} + \text{polyether} \xrightarrow{-45^\circ} B_3H_7\cdot\text{polyether} + {}^1/_2B_2H_6$$

(5) **Mass Spectral Data on the Isotopic Composition of the Diborane Evolved during the Reaction of $NaBD_4$ and B_4H_{10}.**—The B_2H_6 from a $NaBD_4$–B_4H_{10} reaction was recovered from the reaction tube (−45°) by distillation through a −95° trap and condensation in a −196° trap. The B_2H_6 was maintained at −196° until the mass spectrum was run (time elapsed during determination of spectrum did not exceed 2 min.).

An equimolar mixture of B_2D_6 and B_2H_6 was frozen into a tube at −196°, then analyzed on the mass spectrometer to check for equilibration in the instrument. That complete equilibration did not occur is demonstrated by the data in column 5 of Table II. Another equimolar mixture of B_2H_6 and B_2D_6 was equilibrated by allowing it to stand for 12 hr. at room temperature prior to analy-

---

[5] R. W. Parry, D. R. Schultz, and P. R. Girardot, *J. Am. Chem. Soc.*, **80**, 2 (1958).

[6] The importance of maintaining a completely uniform reaction temperature of −45° throughout the vessel was demonstrated by a preliminary experiment in which KBD_4 was allowed to react with B_4H_{10} in diethyl ether at 0°. The resulting triborohydride product approached the composition $KB_3H_6D_2$ rather than KB_3H_7D. The high percentage of deuterium in the product was attributed to side exchange reactions involving products and reactants at the higher temperature. Such an interpretation is reasonable since Todd and Koski [*J. Am. Chem. Soc.*, **81**, 2319 (1959)] found exchange between gaseous B_2D_6 and B_4H_{10} at 25°. Similar exchange in solution between D_3BBH_3, produced in the reaction, and B_4H_{10} which had not yet reacted would give high deuterium content in the solid product. Other similar exchange processes could also give the same result. In every case such reactions complicate the interpretation of the data.

[7] This procedure for separation of $NaBD_4$ and NaB_3H_8 was tested in two preliminary experiments using known and approximately equal amounts of $NaBD_4$ and NaB_3H_8. The solids were dissolved in polyether (Ansul 121); the ether was removed; then diethyl ether was added. The diethyl ether insoluble fraction gave up 96% of the theoretical hydrogen corresponding to the $NaBD_4$ used and the diethyl ether soluble fraction gave up 100% of the hydrogen corresponding to the NaB_3H_8 used. Mass spectrographic analysis of the H_2 from NaB_3H_8 showed only 0.6 atom % D in the evolved gas. In a blank run using $NaBD_4$ and NaB_3H_8 in polyether at −45°, under conditions identical with those used in the run, the separated NaB_3H_8 showed only 0.4 atom % D. Clearly exchange is negligible.

On the other hand, when 1 mole of B_2H_6 was added for each mole of $NaBD_4$ and NaB_3H_8, some exchange did occur. After equilibration of this mixture for 54 hr. at −45°, 4.8% of the hydrogen in the NaB_3H_8 was deuterium. Exchange conditions used here are much more severe than those in the standard $NaBD_4$–B_4H_{10} run since in the exchange study 1 mole of B_2H_6 was present for each mole of NaB_3H_8 throughout the 54-hr. period. In the $NaBD_4$–B_4H_{10} reaction, the concentration of B_2H_6 and NaB_3H_8 started from a low value and built up gradually. Despite these differences the concentration of D in the exchange process was less than half of that in the $NaBD_4$–B_4H_{10} system. The exchange of hydrogen must occur through the direct interaction process; not by an exchange between $NaBD_4$ and NaB_3H_8.

TABLE I

THE REACTION BETWEEN $NaBD_4$ AND NaB_3H_8 IN ETHYLENE GLYCOL DIMETHYL ETHER AT −45°

	Starting materials		Conditions		Products		
	Reagent	Quantity, mmoles	Time, hr.	Temp., °C.	Compd.	Quantity, mmoles	Atom % D
(1)	B_4H_{10}	1.66	36	−45	B_2H_6	1.36	44
	$NaBD_4$	0.958	10	−45 to −5	NaB_3H_8	...	10
	Ether (Ansul 121)	7 ml.			H_2	0.003	...
(2)	B_4H_{10}	0.974			B_3H_6	1.05	45
	$NaBD_4$	0.703	57	−45	NaB_3H_8	...	12
	Ether (121)	4 ml.			H_2	0.04	...
(3)	B_4H_{10}	0.863			B_2H_6	0.802[a]	49.1
	$NaBD_4$	0.869	65	−45	NaB_3H_8	0.784	10
	Ether (121)	7 ml.			H_2	None	
(4)	$NaBD_4$ in runs 1 + 2						96
	$NaBD_4$ in run 3						93.4

[a] A very small amount of additional B–H containing material was detected in the residual ether, after B_2H_6 separation. This could account for the 0.06 mole of material which is missing. Run 3 was carefully conducted to check stoichiometry.

TABLE II

RELATIVE PEAK HEIGHT OF SAMPLES[b]

Mass no.	Pure B_2H_6	Pure B_2D_6	B_2H_6–B_2D_6 25°, 6 hr.	B_2H_6–B_2D_6[a]	B_2H_6–B_2D_6 polyether −45°, 63 hr.	B_2H_6–B_2D_6 mixture from reaction
25	56.1	34.4	88.4	56.6	88.4	85.0
26	100.0	68.5	79.5	100.0	75.1	74.3
27	96.9	13.3	76.8	66.0	73.1	64.7
28	2.3	28.9	100.0	22.4	97.2	93.5
29	...	28.4	98.7	21.5	100.0	100.0
30	...	58.3	72.5	36.3	72.1	81.4
31	...	47.2	36.5	33.0	31.9	41.0
32	...	100.0	9.8	55.9	6.7	9.9
33	...	...	...	...	...	...

[a] This mixture of B_2H_6 was frozen at −196° and allowed to vaporize directly into the mass spectrometer without further equilibration. [b] Mass spectra were determined with a Consolidated Electrodynamics Model 21-103B mass spectrometer at an ionizing voltage of 70 e.v.

sis; a third equimolar mixture was allowed to stand for 63.5 hr. at −45° in contact with polyether. After low temperature fractionation, the mass spectrum of the diborane recovered from the polyether mixture was obtained. The data are summarized in Table II. It is clear that the B_2H_6–B_2D_6 mixture evolved from the reaction has been equilibrated (columns 4 and 7). It is also established by the data in column 6 that a mixture of B_2H_6–B_2D_6 held for 63 hr. at −45° in the presence of polyether is equilibrated. Since the $NaBD_4$–B_4H_{10} reaction was conducted in polyether, the evolved B_2H_6–B_2D_6 mixture should be equilibrated. The data in columns 4, 6, and 7 clearly validate this postulate.

Discussion

If tetraborane is cleaved symmetrically in its reaction with 96% deuterated $NaBD_4$, the NaB_3H_7D should contain 11.5 atom % D and the $B_2H_3D_3$ 48 atom % D. The results in Table I are clearly consistent with symmetrical cleavage. It is also significant that in the last run (stoichiometry carefully followed) no detectable H_2 was evolved and 98% of the added deuterium was recovered, indicating no detectable side reactions. It is difficult to rationalize these results with a nonsymmetrical cleavage mechanism. Sodium triborohydride contains one deuterium atom per formula weight (NaB_3H_7D). Although $NaBD_4$ and NaB_3H_8 do undergo slow exchange in polyether at −45° when excess diborane is present (footnote 7), the rate of exchange, even under the most favorable conditions, is not adequate to explain the results obtained. Transfer of hydrogen during a step (or steps) of the reaction between $NaBD_4$ and B_4H_{10} is clearly indicated.

Although other undefined exchange processes between the deuterated diborane and NaB_3H_8 might be postulated to explain the analysis, it is difficult to believe that such exchange would always go just enough to give an analysis which is consistent with symmetrical cleavage, even though reaction times were varied widely. Symmetrical cleavage seems clearly indicated under the conditions used here.

While the question of cleavage pattern for B_4H_{10} in this reaction can now be answered with some confidence on the basis of the above data, detailed mechanistic questions still remain. The known tendency of ethers to cleave tetraborane symmetrically at room temperature[8] suggests that the initial step in the process might well be the cleavage of the tetraborane by ether at −45°. On the other hand, Kodama and Parry[9] suggested that B_4H_{10} dissolves in diethyl ether at −112° without cleavage since under these conditions tetraborane is attacked by NH_3 to give the nonsymmetrical cleavage product, $[H_2B(NH_3)_2][B_3H_8]$, instead of the symmetrical cleavage products H_3NBH_3 and $H_3NB_3H_7$.

Tetraborane is strikingly similar to diborane in much of its chemistry because of the H_2B units bound to the rest of the molecule by double hydrogen bridges. For this reason observations by Gaines[10] on the ^{11}B n.m.r. spectra of diborane dissolved in either diethyl ether or ethylene glycol dimethyl ether at various temperatures provide significant clues as to the nature of tetraborane–ether solutions. Gaines found that the ^{11}B spectrum

---

(8) L. J. Edwards, W. V. Hough, and M. D. Ford, Memoires a' la Section de Chimie Minerale, XVI Congress International Union of Pure and Applied Chemistry, Paris, 1957, p. 475.

(9) G. Kodama and R. W. Parry, *J. Am. Chem. Soc.*, **82**, 6250 (1960).

(10) D. F. Gaines, *Inorg. Chem.*, **2**, 524 (1963).

of diborane in diethyl ether solution at and below −26° was the same as that of neat diborane; $J_{BH_2} = 135 \pm 2$ c.p.s., $J_{BHB} = 46 \pm 2$ c.p.s. The earlier postulate[9] that tetraborane dissolves in diethyl ether at −112° without cleavage would be consistent with this observation. As the temperature of the B_2H_6 diethyl ether solution was raised, Gaines found that the spectrum of B_2H_6 collapsed, reversibly, first to a broad singlet at 30°, then was resolved into a seven-line multiplet at 84°. The seven-line multiplet was also observed in the polyether at room temperature. Cooling an ethylene glycol dimethyl ether solution of diborane showed the same trends as were observed in the diethyl ether solutions, except that transitions in polyether solutions occurred at much lower temperatures than did those in diethyl ether systems. For example the ^{11}B spectrum of a polyether solution of B_2H_6 at −56° was a triplet, each member of which showed incipient resolution into another triplet.[10] Such a pattern was observed in diethyl ether solution at about 11° and suggests a system containing B_2H_6 molecules undergoing slow exchange through opening of the double bridge. A slow preliminary symmetrical cleavage of the tetraborane molecule by polyether at −45° would then seem eminently reasonable.

If one assumes symmetrical cleavage of tetraborane at −45° by ethylene glycol dimethyl ether, the following reaction sequence would be expected.

$$B_4H_{10} + 2CH_3OCH_2CH_2OCH_3 \longrightarrow B_3H_7\cdot\text{ether} + BH_3\cdot\text{ether} \quad (1)$$

$$B_3H_7\cdot\text{ether} + BD_4^- \longrightarrow DB_3H_7^- + D_3B\cdot\text{ether} \quad (2)$$

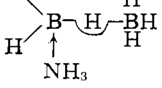
$$H_3B\cdot\text{ether} + D_3B\cdot\text{ether} \longrightarrow B_2H_3D_3 + 2\text{ether} \quad (3)$$

$$H_3B\cdot\text{ether} + H_3B\cdot\text{ether} \longrightarrow B_2H_6 + 2\text{ether} \quad (4)$$

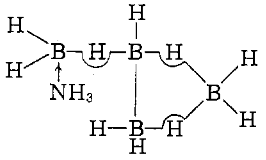
$$D_3B\cdot\text{ether} + D_3B\cdot\text{ether} \longrightarrow B_2D_6 + 2\text{ether} \quad (5)$$

Since it has been established that a mixture of B_2H_6 and B_2D_6 undergoes hydrogen isotope equilibration when allowed to stand for 63 hr. at −45° in the presence of polyether (Table II), one would properly expect an equilibrated mixture of B_2H_6 and B_2D_6 as a product of this reaction. Indeed an equilibrated mixture was obtained and the correct amount of B_2H_6 was evolved at −45° from a control solution of tetraborane in polyether which contained no $NaBD_4$ (eq. 1 and 4).

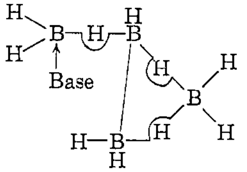
By applying Kodama's[11] extension of the hypothesis of Parry and Shore,[12] a more detailed and flexible mechanism can be proposed which is consistent with all of the available information. In a study of the reaction of B_2H_6 with liquid ammonia it was proposed in this laboratory[12] that one of the two hydrogen bridge bonds of B_2H_6 opens up to give a single bridge bond intermediate.



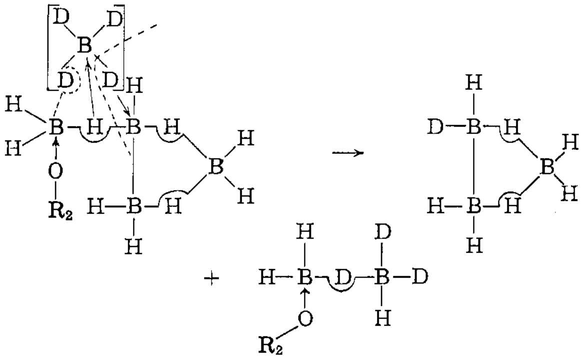
It was suggested that this intermediate would then be attacked very slowly by a second molecule of ammonia at a temperature of −78° to give the nonsymmetrical cleavage product. Base attack on this intermediate would be more rapid at higher temperatures. Kodama[11] applied the above concepts to an interpretation of the reaction between tetraborane and ammonia and suggested the comparable tetraborane intermediate.



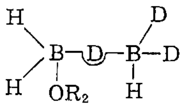
Expanding this concept to generalized reactions between bases and tetraborane, one could postulate that all bases, those giving symmetrical as well as those giving nonsymmetrical cleavage, form an intermediate of the general form



The nature of the subsequent attacking nucleophile, as well as the nature of the base attached to the H_2B– group, would then determine whether a symmetrical or nonsymmetrical cleavage product is obtained. In the ether solution of this study the base attached to the H_2B– group would be an ether molecule. The specific attack of BD_4^- on this intermediate can be pictured as



In this model one deuterium and its associated electron pair would move to the B_3H_7 fragment to give the observed $B_3H_7D^-$ ion. The single bridge hydrogen of B_4H_{10} would then move up to the boron of the borohydride and a single deuterium bridge would join the etherated BH_3 fragments together.



Such a model would account for the presence of about 11% D in the $B_3H_8^-$ and in part for the equilibrated B_2H_6–B_2D_6 mixture obtained from the solution.

The model would also explain the evolution of B_2H_6

---

[11] G. Kodama, Ph.D. Dissertation, University of Michigan, 1957, p. 54.

[12] R. W. Parry and S. G. Shore, *J. Am. Chem. Soc.*, **80**, 15 (1958).

in the absence of BH_4^- since slow attack of ether (a symmetrical cleavage agent) on the B_4H_{10}–R_2O intermediate would give H_3BOR_2 and $H_7B_3OR_2$. The former product would equilibrate with gaseous diborane above the solution. Removal of such gaseous B_2H_6 would drive the reaction to completion.

Furthermore, the possibility of unsymmetrical cleavage through the action of other reagents on this intermediate would not be eliminated. For example, OH^- or NH_2^-, which are known to favor unsymmetrical cleavage,[13] might well be expected to react on the intermediate to give unsymmetrical cleavage products (*i.e.*, $B_3H_8^-$ and H_2BOHOR_2).

Acknowledgment.—The support of this work by the National Science Foundation under grants NSF-G10372 and NSF-G21408 is gratefully acknowledged.

(13) R. W. Parry and L. J. Edwards, *J. Am. Chem. Soc.*, **81**, 3559 (1959); P. F. Winternitz, ref. 3, p. 178.

CONTRIBUTION FROM MONSANTO RESEARCH CORPORATION,
DAYTON LABORATORY, DAYTON, OHIO 45407

Oxidation of Methylboranes at 77–170°K.

BY L. PARTS AND JOHN T. MILLER, JR.

Received February 7, 1964

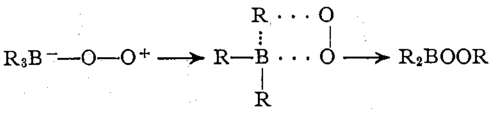
The oxidizability of $(CH_3)_3B$ (at 77 and 90°K.), 1,1-$(CH_3)_2B_2H_4$ (at 90°K.), $(CH_3)_4B_2H_2$ (at 170°K.), B_2H_6 (at 77°K.), and $(CH_3)_3P$ (at 147°K.) has been investigated in solution. Of these compounds only trimethylborane was found to be susceptible to oxidation, yielding dimethylboryl methyl peroxide in coordination polymeric form. Depolymerization to monomeric peroxide occurs upon warming. The results are consistent with a mechanism that involves transitory formation of an acid–base type adduct of trimethylborane with oxygen. The latter rearranges even at 77°K. to dimethylboryl methyl peroxide, $(CH_3)_2BOOCH_3$. A glass-and-metal high vacuum system was designed for low-temperature studies.

The susceptibility of boron alkyls to autoxidation is well known and the formation of peroxides,[1–6] boronates, borinates, and borates in the oxidative processes has been established. Brief discussions of this work with pertinent references, and of the mechanism of oxidation, have appeared in recent books.[7,8]

It has generally been assumed, following the initial suggestion by Johnson and Van Campen[9] and in analogy with the proposed mechanism of the oxidation of organomagnesium compounds,[10,11] that the primary step of oxidation involves the formation of a coordinate bond between the boron atom and oxygen.

$$R_3B + O_2 \longrightarrow R_3B^{-}\text{—O—O}^{+} \qquad (1)$$

Subsequent intramolecular migration of the alkyl group from boron to oxygen[3] has been proposed to yield the peroxides.



$$R_3B^{-}\text{—O—O}^{+} \longrightarrow \underset{R}{\overset{R\,\cdots\,O}{R\text{—B}\cdots O}} \longrightarrow R_2BOOR \qquad (2)$$

The inhibition of autoxidation by propylamine,[3] the lowering of reactivity upon vinyl substitution,[12] and the ineffectiveness of free radical trapping agents[3] are experimental findings which support the argument for the molecular mechanism of trialkylborane oxidation *in solution*. Reported experimental evidence for the existence of an oxygen coordination compound with tri-*n*-butylborane at 299°K.[4] could not be confirmed.[5]

The mechanism, which is consistent with the results of kinetic measurements on *gas phase* oxidation of trimethylborane, involves a radical chain reaction, initiated and terminated at the wall.[13,14]

It was thought to be of interest to investigate the oxidation of trimethylborane in solution at cryogenic temperatures. The energy of activation for the coordinate bond formation (reaction 1) can be assumed to be nearly zero. If the coordinate bond strength exceeds a few kcalories and the intramolecular rearrangement (reaction 2) is an activated process with a sufficiently high energy barrier ($E_{act} > 5$ kcal./mole), the oxidation could be halted at 77°K. after formation of the oxygen adduct. The exponential dependence of reaction rates upon temperature facilitates the preparation and study of metastable reaction intermediates at cryogenic temperatures.

It was also considered to be of interest to compare the autoxidative susceptibility of trimethylborane and of methylated diboranes under conditions which would not be expected to lead to oxidation reactions by a free

(1) R. C. Petry and F. H. Verhoek, *J. Am. Chem. Soc.*, **78**, 6416 (1956).

(2) R. C. Petry, Ph.D. Dissertation, The Ohio State University, 1958.

(3) M. H. Abraham and A. G. Davies, *Chem. Ind.* (London), 1622 (1957).

(4) N. L. Zutty and F. J. Welch, *J. Org. Chem.*, **25**, 861 (1960).

(5) A. G. Davies, D. G. Hare, and O. R. Khan, *J. Chem. Soc.*, 1125 (1963).

(6) R. L. Hansen and R. R. Hamann, *J. Phys. Chem.*, **67**, 2868 (1963).

(7) W. Gerrard, "The Organic Chemistry of Boron," Academic Press, London and New York, 1961, p. 114.

(8) H. C. Brown, "Hydroboration," W. A. Benjamin, Inc., New York, N. Y., 1962, p. 67.

(9) J. R. Johnson and M. G. Van Campen, Jr., *J. Am. Chem. Soc.*, **60**, 121 (1938).

(10) C. Walling and S. A. Buckler, *ibid.*, **75**, 4372 (1953).

(11) C. Walling and S. A. Buckler, *ibid.*, **77**, 6032 (1955).

(12) T. D. Parsons, M. B. Silverman, and D. M. Ritter, *ibid.*, **79**, 5091 (1957).

(13) C. H. Bamford and D. M. Newitt, *J. Chem. Soc.*, 695 (1946).

(14) J. E. Coleman, Ph.D. Dissertation, The Ohio State University, 1959.