We have no explanation for the discrepancy, and Mochalov, *et al.*, gave no experimental details to aid in seeking an explanation.

The Monohydroboron Species.—In both nonbuffered strongly acidic solutions and strongly alkaline solutions we observed pH-independent rates of hydrolysis of the monohydroboron species. At 0°, the pseudo-first-order rate constant is 4.4×10^{-3} sec^{-1} in acidic solutions and is 1.0×10^{-3} sec^{-1} in alkaline solutions. Although the rate constants are of similar magnitude, they probably correspond to the hydrolyses of different species. We believe that the species in acidic solutions is $H_2OBH(OH)_2$ and that the species in alkaline solutions is $BH(OH)_3^-$. In buffer solutions of pH 5.6 and 10.0, the rate of hydrolysis of the monohydroboron species was found to be about twice that in acidic solutions. Perhaps this rate increase was due to reaction of $BH(OH)_3^-$ with the acid component of the buffer solution.

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The Asymmetric Cleavage of Diborane by Water. The Structure of Diborane Dihydrate

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The dihydrate and diethanolate of diborane have been prepared at −130° and their compositions have been established by stoichiometric measurements. The dihydrate is assigned the structure $BH_2(H_2O)_2^+BH_4^-$ on the basis of low-temperature infrared spectra of the deuterated and nondeuterated species. A study of the evolution of hydrogen from the reaction of diborane with a solution of HCl in a water–methanol mixture at −78° has provided further evidence for the asymmetric cleavage of diborane by water and alcohol.

Introduction

The cleavage of the bridging hydrogen bonds in diborane by a Lewis base, X, can be either symmetric, to give BH_3X, or asymmetric, to give $BH_2X_2^+$ and BH_4^-.[1,2] In the reaction of ammonia with diborane, both types of cleavage have been observed.[3,4] With increasing methyl substitution in the methylamine series, there is an increasing tendency for symmetric cleavage.[5-7] Various ethers cleave diborane symmetrically,[8] whereas dimethyl sulfoxide cleaves diborane asymmetrically.[9] Young and Shore[10] have discussed some of the factors which may affect the course of these cleavage reactions; it appears that it is not yet possible to predict the course of such reactions with certainty.

In studies of the reaction of diborane with water[11] and alcohols[12] at room temperature, no intermediate cleavage products have been isolated because complete hydrolysis occurs rapidly. Davis and Gottbrath[13] were able to isolate sodium hydroborate from the reaction of diborane with aqueous sodium hydroxide at 0°, and Jolly and Schmitt[14] prepared potassium hydroborate by the reaction of diborane with powdered potassium hydroxide at −30°. These results are consistent with asymmetric cleavage of diborane and prompted a further study of this type of reaction. This paper describes the preparation and characterization of the initial diborane–water reaction product.

Experimental Section

General Information.—Diborane was prepared by the addition of KBH_4 to H_3PO_4,[15] and deuteriodiborane was prepared by the addition of BF_3 etherate to $LiAlD_4$ in diethyl ether.[16] The purity of both compounds was verified by vapor pressure measurements[17] and infrared spectroscopy.[18] The $LiAlD_4$ (deuterium content 99%) was obtained from Bio-Rad Laboratories, Richmond, Calif., and deuterium oxide (deuterium content 98.8%) from International Chemical and Nuclear Corp., Chemical and Radioisotope Division, Irvine, Calif. All other chemicals were of reagent grade. Ideal gas behavior was assumed for vapors and gases when making calculations from *PVT* data. Low pressures of water, ethanol, and methanol were used to ensure the ideality of their vapors.

Stoichiometric Studies.—The glass reaction vessel was 20 cm long, with three connections (one for evacuation) located at the top. Two $^1/_8$-in. metal tubes, joined to the glass vessel with Swagelock fittings, were suspended next to each other within the vessel with their lower ends 1 cm from the base of the vessel. Nupro gas-metering valves were attached to the upper, outer ends of the tubes.

A 100-fold excess of diborane and either water, ethanol, or

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methanol were cocondensed as an intimate solid mixture by allowing the vapors to separately but simultaneously effuse into the vessel, which was cooled to −196°. The inlet tubes were heated during deposition by heating tape which was wound around the portions above the reaction vessel. The condensed mixture was then warmed to −130° (−112° for the methanol mixture). When the reaction was judged complete (2–3 hr for water, 1 hr for ethanol, and 2–4 hr for methanol), the excess diborane was removed by pumping. A large excess of water was condensed into the vessel and each sample was then warmed to room temperature to effect complete hydrolysis. The amount of diborane which had reacted was calculated by measuring the evolved hydrogen, which had been Toepler-pumped into a gas buret. It was assumed that each mole of diborane consumed in hydrolysis at room temperature produced 6 mol of hydrogen.[19]

The reaction between excess water (280 mmol) and diborane (0.20–0.25 mmol) was studied at −130° to determine the per cent of diborane that reacted as a function of time. Within 15 min, 86% had reacted; after 2 hr, 98% had reacted.

Acid Hydrolysis.—Approximately 25 ml of 0.5 *M* HCl in 88% by volume methanol and 12% by volume water was pipetted into a 70-ml flat-bottomed flask containing a stirring bar. The vessel was cooled to −78° using a Dry Ice–acetone bath and then was evacuated while the solution was stirred and the glass walls were heated. (The heating eliminates droplets which cause excessive decomposition.) Diborane (0.05–0.10 mmol) was introduced into the reaction vessel by momentarily opening a stopcock which connected the vessel with a chamber containing diborane gas at −130°. All unreacted diborane in the entry line was then removed by pumping. The pressure of the evolved hydrogen was measured after 40–90 sec in a constant-volume system consisting of the reaction vessel and an adjustable manometer. The hydrogen pressures for four different runs were 0.30, 0.43, 0.64, and 0.78 cm. These pressures were corrected for the hydrogen evolved by the hydrolysis of any H_2OBH_3 in solution using the first-order rate law $a = a_0e^{-kt}$, where $k = 2.3 \times 10^{-3}$ sec^{-1} at −78° in 0.5 *M* HCl.[20] The corrected hydrogen pressures were 0.27, 0.39, 0.58, and 0.67 cm, respectively, assuming that the diborane reacted immediately as follows: $B_2H_6 + 3H_2O = BH_2(H_2O)_2^- + H_2OBH_3 + H_2$.

After approximately 40 min, the total pressure of evolved hydrogen was measured. These hydrogen pressures were 0.80, 1.11, 1.41, and 1.45 cm, respectively. The reaction vessel was then isolated from the system and warmed to room temperature to complete hydrolysis. The total pressure of evolved hydrogen was measured in the constant-volume system after recooling the reaction vessel to −78°. The hydrogen pressures were 1.71, 2.41, 2.96, and 3.44 cm, respectively. Because the external temperature varied less than 1° and because care was taken to keep the level of the −78° bath around the reaction vessel constant, the hydrogen pressure measurements could be used to determine the ratio of moles of hydrogen initially evolved (corrected) to moles of diborane consumed (assumed to be equal to one-sixth of the total pressure of evolved hydrogen). These ratios were 0.97, 0.98, 1.18, and 1.18.

Infrared Measurements.—The metal low-temperature infrared cell[21] consisted of an outer shell with CsI windows perpendicular to the optical axis and an inner part which contained the refrigerant (liquid nitrogen). From the inner part was suspended a copper block in which was mounted the CsBr plate upon which the samples were codeposited. The inner part could be rotated relative to the outer shell during the course of the experiment, allowing the CsBr plate to be oriented normal either to the gas inlet system or to the optical axis. The spectra were recorded on a Perkin-Elmer 221 spectrophotometer calibrated with polystyrene.

The temperature of the CsBr plate was not known accurately. The approximate temperature was estimated by measuring the vapor pressure (4 cm at −130°)[17] of the excess diborane at various times during warmup after removal of the liquid nitrogen. It took 1 hr of warming for reaction to occur (∼−140°), and the product remained stable during a further hour of warming (∼−100°).

Gaseous diborane and water vapor were introduced through Nupro metering valves and cocondensed on the CsBr plate cooled to −196°. In different runs, the deposition rates of diborane and water were 1–2 and 3–4 mmol/hr, respectively. The deposition time was 60–90 min. Longer deposition times produced a thick film of low light transmittance.

After deposition, an initial spectrum was taken at −196°. The refrigerant was then removed and the infrared cell was allowed to warm so that the diborane could vaporize and react with the porous, reactive ice. Spectra in the 3000–2000 cm^{-1} region were recorded at 5–10-min intervals during warm-up to follow the course of reaction. The vaporized, unreacted diborane was collected in a −196° trap immediately before each spectrum was run and afterward returned to the system. Within 1 hr, the system was warmed to approximately −140°. The unreacted diborane (80–90%) was removed by pumping, leaving a mixture of diborane dihydrate and ice in a mole ratio of approximately 1:18. The reaction was quenched by the introduction of liquid nitrogen, and a spectrum in the 4000–500-cm^{-1} region was recorded at −196°. The refrigerant was removed, and the infrared cell was allowed to warm gradually. Spectra in the 3000–2000-cm^{-1} region were again taken at 5–10-min intervals while continuously pumping. The peaks diminished with increasing temperature; their complete disappearance coincided with the evolution of a large amount of hydrogen (∼−100°). A final spectrum was run. Reported frequencies are accurate to ±10 cm^{-1}.

Results and Discussion

Stoichiometric Studies.—Because the diborane hydrate and diborane alcoholates decompose when the temperature is high enough to volatilize water, ethanol, or methanol, it was not possible to determine directly the amounts of these reagents that reacted with diborane when they were in excess. Therefore stoichiometric studies were possible only when using excess diborane, which is volatile even at −140°. The results of these studies are summarized in Table I. Diborane was present in at least a 100-fold excess in most of the experiments.

TABLE I

STOICHIOMETRIC STUDIES OF THE LOW-TEMPERATURE REACTIONS OF DIBORANE WITH WATER, ETHANOL, AND METHANOL

	Amt, mmol			H_2O or ROH (mmol)/ B_2H_6 consumed (mmol)
		Diborane		
Reactant	Reactant	Introduced	Consumed	
Water	0.010	3.926	0.0052	1.9
	0.017	4.050	0.0080	2.1
	0.019	3.986	0.0082	2.3
Ethanol	0.055	2.770	0.0243	2.3
	0.069	2.692	0.0307	2.2
	0.027	3.218	0.0143	1.9
	0.032	3.215	0.0150	2.1
	0.023	2.872	0.0123	1.9
	0.026	2.494	0.0150	1.7
Methanol	0.060	2.617	0.035	1.7
	0.100	3.311	0.062	1.6

The diborane hydrate is relatively stable; only 3% decomposition[22] occurred in 1 hr at −112°. Both alcoholates, however, are much more unstable. In 1 hr at −130° 25% decomposition[22] of the ethanolate occurred. Decomposition is negligible at −160°; however, studies were not conducted at this temperature because excess diborane cannot be removed by pumping. In the case of the diborane methanolate, 50% decomposition[22] occurred in 2–4 hr at −112°.

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For both the diborane–water and the diborane–ethanol reactions, approximately 2:1 molar ratios were found at −130° for $H_2O:B_2H_6$ and $C_2H_5OH:B_2H_6$. A lower ratio, 1.7:1, was found for the methanol–diborane system. We have no explanation for this low result, except the fact that the methanol reaction was studied at a relatively high temperature.

Hydrolysis Study.—The stepwise hydrolysis of hydroborate in acidic solution at −78° has been followed kinetically.[20] In the first step, 1 mol of hydroborate reacts essentially instantaneously to produce H_2OBH_3 and 1 mol of hydrogen.

$$BH_4^- + H^+ + H_2O \longrightarrow H_2OBH_3 + H_2 \qquad (1)$$

The second step proceeds more slowly (half-time approximately 5 min at −78° in 0.5 *M* acid) and produces a second mol of hydrogen and $BH_2(H_2O)_2^+$.

$$H_2OBH_3 + H_2O + H^+ \longrightarrow BH_2(H_2O)_2^+ + H_2 \qquad (2)$$

The species $BH_2(H_2O)_2^+$ is relatively stable in acidic solution (the greater the acidity, the more stable), and further hydrolysis occurs only when the temperature is increased or during prolonged standing (3–4 hr).

$$BH_2(H_2O)_2^+ + H_2O \longrightarrow B(OH)_3 + H^+ + 2H_2 \qquad (3)$$

We observed the reaction of diborane with 0.5 *M* HCl in 88% methanol by volume and 12% water by volume. If H_2OBH_3 were the initial product, hydrogen evolution would be gradual; in 40 min (about 8 half-times) almost 2 mol of hydrogen would be produced per mole of diborane. If $BH_2(H_2O)_2^+$ and BH_4^- were the initial reaction products, 1 mol of hydrogen/mol of diborane would be evolved instantaneously (eq 1), and a second mole of hydrogen would be evolved during the following 40 min (eq 2). The latter results were actually observed. Therefore we conclude that the initial reaction products are $BH_2(H_2O)_2^+$ and BH_4^-.

Spectra.—The spectrum of the diborane–water mixture which had never been warmed above −196° consisted of the superimposed spectra of diborane and water. While warming the mixture, the diborane spectrum gradually disappeared and the product spectrum gradually appeared. After removal of the unreacted diborane from the system by pumping, the system was cooled to −196° and a clean (no unreacted diborane) spectrum of the product was obtained. When the material was again warmed, for a longer time and hence to a higher temperature, the compound gradually decomposed. The final spectrum was that of boric acid.[23] No other species were observed. In Figure 1 are presented the initial spectrum of the reactants, the spectrum of diborane dihydrate plus excess water, and the final spectrum of boric acid and water. Similar spectral studies were carried out with deuteriodiborane and deuterium oxide using the same experimental procedure, and completely analogous results were obtained. The major infrared absorption frequencies and their assignments are listed in Table II for the diborane dihydrate and in Table III for the deuterated species.

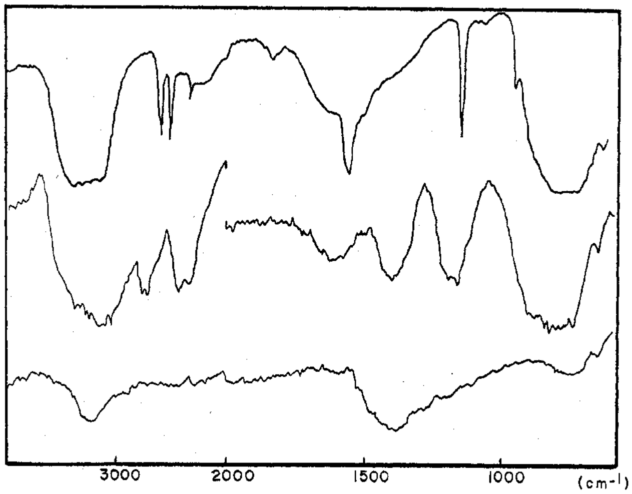

Figure 1.—The initial spectrum of the reactants, the spectrum of diborane dihydrate plus excess water, and the final spectrum of boric acid and water.

TABLE II

INFRARED ABSORPTION FREQUENCIES OF DIBORANE DIHYDRATE

ν, cm^{-1}	Intens	Assignment
3200	vs	OH str
2750, 2720	s	BH str, $BH_2(H_2O)_2^+$
2420	s	BH str, BH_4^-
2320	s	BH str, BH_4^-
1605	m	OH def
1400	s	BO str
1185	s	BH def, BH_4^-
1155	s	BH def, $BH_2(H_2O)_2^+$

TABLE III

INFRARED ABSORPTION FREQUENCIES OF DEUTERATED DIBORANE DIHYDRATE

ν, cm^{-1}	Intens	Assignment
3250	s	OH str (HOD impurity)
2400	vs	OD str
1845	s	BD str, $BD_2(D_2O)_2^+$
1745	m	BD str, BD_4^-
1700	m	BD str, BD_4^-
1350	vs	BO str
1085	s	OD def
885	s, sh	BD def, BD_4^-
855	s	BD def, BD_4^-
745	m	BD def, $BD_2(D_2O)_2^+$

The diborane dihydrate spectrum shows six strong bands that can be attributed to B–H bonds—four bands in the 2800–2300-cm^{-1} region (due to B–H stretching modes) and two bands in the 1200–1100-cm^{-1} region (due to H–B–H deformation modes). Adducts of the type BH_3X show only three B–H bands—two due to B–H stretching modes and one due to H–B–H deformation.[24–26] Consequently diborane dihydrate cannot have a simple H_2OBH_3 structure. We believe that the infrared spectrum can be best interpreted in terms of the $BH_2(H_2O)_2^+BH_4^-$ structure. Salts containing cations of the type $BH_2X_2^+$ show a doublet in the 2600–2400-cm^{-1} region corresponding to B–H stretching and a single band in the 1200–1100-cm^{-1} region corresponding to H–B–H deformation.[27–29] Hydroborates typically show a peak with two shoulders[30] or three

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bands[31-33] in the 2400–2200-cm^{-1} region and a single band in the H–B–H deformation region.[30-33] Thus the six bands of diborane dihydrate can be accounted for by assuming the presence of $BH_2(H_2O)_2^+$ and BH_4^-.

The assignment of the high-frequency doublet in the dihydrate spectrum (with peaks at 2750 and 2720 cm^{-1}) to the $BH_2(H_2O)_2^+$ ion deserves some comment. These frequencies are about 150 cm^{-1} higher than those previously found for the B–H stretching in $BH_2X_2^+$ salts.[27-30] However, all the $BH_2X_2^+$ salts which have been previously studied have had X ligands which are relatively strong donors, usually with donor atoms less electronegative than oxygen. In $BH_2(H_2O)_2^+$, the high electronegativity of the oxygen atoms causes the boron orbitals used in the B–O bonds to have a high degree of p character. Consequently the boron orbitals used in the BH bonds have a high degree of s character, and the BH bonds are extraordinarily strong and have a very high stretching frequency.[34] We may similarly argue that the water molecules in $BH_2(H_2O)_2^+$ are relatively poor donor molecules and that consequently the BH bonds are more nearly like those in free BH_2^+. In the latter species the boron orbitals would be sp-hybrid orbitals and the B–H bonds would be stronger than those in which the boron is essentially sp^3 hybridized.

The ν_H/ν_D ratios for the BH_4^- bands have normal values—1.39, 1.36, and 1.39—and, as expected, the B–O stretching frequency was essentially unaffected by deuteration. The ν_H/ν_D ratios for the $BH_2(H_2O)_2^+$ bands are somewhat high (1.48 and 1.55) but not unreasonable.

A similar infrared study of the B_2D_6–H_2O system yielded little information because the broad H_2O deformation band in the 1700–1600 cm^{-1} region obscured the B–D stretching bands of BD_4^-. A band was observed at 1850 cm^{-1}, as well as a weak band near 2700 cm^{-1}, presumably due to $BD_2(H_2O)_2^+$ and $BH_2(H_2O)_2^+$, respectively. Perhaps the latter species can be accounted for by a small amount of hydrogen–deuterium exchange.

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Notes

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The Reaction of Heptasulfur Imide with Diborane

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It is known that heptasulfur imide reacts with boron trichloride and boron tribromide to give S_7NBCl_2[1] and S_7NBBr_2,[2] respectively. In this note we report the results of our study of the reaction of heptasulfur imide with diborane. This study was undertaken to determine whether the reaction gives an analogous product (S_7NBH_2), a borane adduct ($S_7NH \cdot BH_3$), or a diborane derivative such as $S_7NB_2H_5$.

Results and Discussion

The reaction of heptasulfur imide with diborane was carried out in various ether solvents, at either room temperature or 0°. The experimental results, summarized in Table I, show that, with diborane in excess, 0.5 mol of diborane reacts per mole of S_7NH and that 1 mol of hydrogen is formed per mole of S_7NH. This stoichiometry corresponds to the reaction $S_7NH + 0.5B_2H_6 \rightarrow S_7NBH_2 + H_2$.

TABLE I
STOICHIOMETRY OF THE REACTION OF S_7NH WITH B_2H_6

Solvent	Temp, °C	Amt, mmol S_7NH	Amt, mmol B_2H_6	Measd H_2/S_7NH	Time of meas, hr	B_2H_6 consumed/ S_7NH
Monoglyme[a]	23	0.288	0.41	1.11[b]	17	0.49
Monoglyme	23	0.992	0.72	1.35[b]	64.5	...
Monoglyme	0	0.574	0.516	1.0[c]	66	0.495
	23			1.15[b]	24	
THF[a]	23	0.386	0.356	0.99	67	0.505
THF	23	0.616	0.50	1.13[b]	65.5	...
THF	23	0.567	0.264	1.09[b,d]	145	...
THF	0	0.611	0.593	1.02	497	0.52
THF	0	0.302	0.0716	1.31[b,d]	978	...
Dioxane	23	0.505	0.633	2.20[b]	319	...
Diethyl ether[a]	0	0.575	0.292	0.98	260	...

[a] Reaction mixture not stirred. [b] Traces of H_2 still being evolved, due to slow decomposition. [c] Stopped purposely to pump out excess B_2H_6. [d] Listed as H_2/B_2H_6.

When the reaction is carried out in diethyl ether at 0°, some of the product precipitates as a white, crystalline ether adduct, $S_7NBH_2 \cdot Et_2O$. Similar adducts can be obtained from the other ethers by vacuum evaporation of the solvent and removal of excess diborane. The compounds undergo rapid hydrolysis with excess water at room temperature: $S_7NBH_2 \cdot \text{ether} + 3H_2O \rightarrow S_7NH + B(OH)_3 + 2H_2 + \text{ether}$.

The ^{11}B nmr spectrum of S_7NBH_2 in diethyl ether solution consists of a 1:2:1 triplet due to coupling with the two protons of the BH_2 group. The Raman spectrum of the diethyl ether adduct has lines at 2419 and 2409 cm^{-1}, characteristic of terminal BH_2 groups, and lines at 766 and 750 cm^{-1}, typical S–N stretching frequencies.

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