CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF ARIZONA, TUCSON, ARIZONA 85721

Reactions of Amine Hydrochlorides with Lithium Bis(borane)dimethylphosphide(1−). Synthesis and Properties of Compounds with N–B–P–B Backbones

BY LAWRENCE D. SCHWARTZ AND PHILIP C. KELLER*

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Reactions of $Li(CH_3)_2P(BH_3)_2$ with tri-, and di-, and monomethylammonium chloride and ammonium chloride produce hydrogen and the compounds (amine)–BH_2–$P(CH_3)_2$–BH_3. The new materials have been characterized by their infrared, boron-11 and proton nmr, and mass spectra. Pyrolysis generates $[(CH_3)_2PBH_2]_3$ and products characteristic of the thermal decomposition of the appropriate amine–borane.

A recent paper from this laboratory[1] described the reactions (eq 1) of amine hydrochlorides with $Na(CH_3)_2N(BH_3)_2$ to form the previously known amine adducts of μ-$(CH_3)_2NB_2H_5$.[2] The natural extension of this

$$(\text{amine})H^+ + (CH_3)_2N(BH_3)_2^- \longrightarrow H_2 + (\text{amine})\text{–}BH_2\text{–}N(CH_3)_2\text{–}BH_3 \quad (1)$$

$$(\text{amine} = (CH_3)_3N,\ (CH_3)_2NH,\ CH_3NH_2,\ NH_3)$$

work to the reactions of amine hydrochlorides with $Li(CH_3)_2P(BH_3)_2$[3] to form new compounds with N–B–P–B backbones is the subject of this article.

Experimental Section

General Data.—Standard high-vacuum and inert-atmosphere techniques[4] were used for all manipulations. Boron-11 and proton nmr spectra were obtained using a Varian HA-100 spectrometer operating at 32.1 and 100 MHz, respectively. Boron chemical shifts are expressed in ppm relative to $(C_2H_5)_2O\cdot BF_3$. Infrared spectra were obtained using Perkin-Elmer 137 and 337 spectrophotometers. Mass spectra were produced by a Hitachi Perkin-Elmer RMU-6E double-focusing spectrometer.

The pure solvents monoglyme (1,2-dimethoxyethane), toluene, dioxane, and benzene were stored in evacuated bulbs over lithium aluminum hydride and, when needed, were condensed directly into the reaction vessel. The $(CH_3)_3NHCl$, $(CH_3)_2NH_2Cl$, CH_3NH_3Cl, and NH_4Cl were reagent grade purchased from commercial sources and were used without further purification. The $Li(CH_3)_2P(BH_3)_2\cdot C_4H_8O_2$ was prepared as previously described.[3]

Analysis was accomplished by preliminary acid hydrolysis; hydrolytic hydrogen was collected and measured with a Toepler pump–gas buret assembly. Phosphorus was determined by recovery of dimethylphosphine on the vacuum line following adjustment of the acidity of the hydrolysis solution to approximately pH 6. Nitrogen was determined by a Kjeldahl-type procedure and boron was estimated by titration of the boric acid D-mannitol complex with standard base.

General Preparative Method.—In a typical reaction a 100-ml vessel was charged with 1–2 mmol of $Li(CH_3)_2P(BH_3)_2\cdot C_4H_8O_2$ and a 10–15% excess of the appropriate amine hydrochloride. About 5 ml of monoglyme was condensed into the vessel and the solution was stirred magnetically and maintained at 60–65° for 12 hr. Hydrogen produced during this period usually amounted to 100–105% of that required for reaction 2. Following removal

$$(\text{amine})H^+ + (CH_3)_2P(BH_3)_2^- \longrightarrow H_2 + (\text{amine})\text{–}BH_2\text{–}P(CH_3)_2\text{–}BH_3 \quad (2)$$

of the solvent and dioxane on the vacuum line, the product was isolated by sublimation at 50°. Yields were generally on the order of 70%. The monomethylamine and ammonia derivatives were often contaminated by a small quantity of an unidentified oil which could be removed by washing the product with cold, dry *n*-heptane.

Pyrolysis reactions were carried out in sealed Pyrex vessels at temperatures ranging from 150 to 240°. After separation, the products were identified by their infrared and mass spectra.

Characterization of $(CH_3)_3N$–BH_2–$P(CH_3)_2$–BH_3.—Elemental analyses were as follows. *Anal.* Calcd: B, 14.7; hydridic H, 3.40; N, 9.51; P, 21.1. Found: B, 14.9; hydridic H, 3.60; N, 9.39; P, 20.7. The product was obtained as air-stable colorless crystals, mp 48–49°, which were soluble in benzene, monoglyme, acetone, dioxane, and ethanol and insoluble in water. Boron-11 nmr (C_6H_6, Figure 1): quartet δ 6.2 ppm (J = 86 Hz), quartet of doublets δ 35.2 ppm (J_{BH} = 93 Hz, J_{BP} = 57 Hz); proton nmr (C_6H_6): singlet τ 7.74 (intensity 3), doublet τ 9.02 (J_{PCH} = 4.8 Hz, intensity 2); monoisotopic mass spectrum (70 eV) [*m/e* (relative intensity)]: 147 (3), 146 (13), 145 (9), 144 (6), 141 (6), 134 (9), 133 (85), 132 (19), 118 (3), 117 (6), 116 (1), 98 (3), 97 (1), 89 (6), 88 (4), 86 (6), 75 (5), 74 (3), 73 (10), 71 (100), 71 (11), 70 (42), 69 (10), 68 (4), 67 (3), 62 (6), 61 (3), 60 (2), 59 (19), 58 (37), 57 (8), 56 (20), 55 (7), 54 (5), 46 (7), 45 (5), 44 (5), 43 (4), 42 (12), 41 (16), 40 (8), 39 (4), 30 (10), 29 (6), 28 (12), 27 (16), 26 (7); ir (KBr) in cm^{-1} (relative intensity): 2950 (m), 2900 (sh, m), 2370 (vs), 2320 (vs), 2220 (sh, s), 2110 (sh, w), 1490 (sh, m), 1470 (s), 1430 (sh, m), 1410 (m), 1293 (w), 1275 (w), 1253 (sh, m), 1243 (m), 1150 (m), 1120 (s), 1080 (s), 1055 (s), 1008 (m), 975 (m), 945 (m), 917 (m), 860 (s), 775 (w), 750 (m), 705 (m), 696 (sh, w), 660 (sh, w), 650 (m), 555 (m), 481 (m).

Products of the complete pyrolysis at 240° for 15 hr were $(CH_3)_3NBH_3$, $[(CH_3)_2PBH_2]_3$, $[CH_3NBH]_3$ (trace), and noncondensable gas, assumed to be methane.

Characterization of $(CH_3)_2NH$–BH_2–$P(CH_3)_2$–BH_3.—Elemental analyses were as follows. *Anal.* Calcd: B, 16.2; hydridic H, 3.76; P, 23.4; mol wt 133. Found: B, 16.1; hydridic; H, 3.57; P, 23.8; mol wt (cryoscopic in C_6H_6) 131. The product was obtained as air-stable colorless crystals, mp 76–77°, which were soluble in benzene, monoglyme, toluene, cyclohexane, and trichloroethylene and insoluble in water. Boron-11 nmr (C_6H_6): quartet δ 9.2 ppm (J = 89 Hz), quartet of doublets δ 36.2 ppm (J_{BH} = 91 Hz, J_{BP} = 64 Hz); proton nmr (C_6H_6): broad singlet τ 4.88 (intensity 1), doublet τ 7.09 (J_{HNCH} = 2.5 Hz, intensity 6), doublet τ 8.94 (J_{PCH} = 5.0 Hz, intensity 6); monoisotopic mass spectrum (70 eV) [*m/e* (relative intensity)]: 133 (5), 132 (24), 131 (13), 130 (5), 129 (2), 128 (5), 127 (4), 121 (1), 120 (15), 119 (63), 118 (100), 117 (9), 116 (9), 115 (3), 114 (8), 113 (3), 104 (7), 103 (10), 102 (3), 89 (5), 88 (2), 87 (3), 86 (2), 85 (2), 84 (6), 83 (5), 82 (3), 75 (25), 74 (14), 73 (9), 72 (13), 71 (4), 70 (11), 69 (9), 68 (6), 67 (1), 66 (5), 63 (15), 62 (73), 61 (9), 60 (2), 59 (17), 58 (61), 57 (62), 56 (18), 55 (31), 54 (9), 53 (4), 52 (6), 48 (4), 47 (6), 46 (37), 45 (42), 44 (60), 43 (6), 42 (35), 41 (32), 40 (17), 39 (8), 30 (19), 29 (10), 28 (22), 27 (26), 26 (14); ir (KBr) in cm^{-1} (relative intensity): 3270 (s), 2995 (sh, w), 2950 (m), 2920 (sh, w), 2760 (w), 2340 (sh, s), 2315 (vs), 2270 (sh, s), 2125 (vw), 1450 (s), 1420 (s), 1310 (w), 1280 (vw), 1260 (m), 1160 (sh, m), 1140 (m), 1080 (s), 1060 (s), 1015 (w), 955 (sh, m), 945 (m), 925 (m), 910 (sh, m), 855 (w), 755 (w), 735 (vw), 715 (m), 660 (w), 640 (vw), 570 (w).

Pyrolysis at 150° for 1 hr resulted in only 20% decomposition based on evolved hydrogen. The products were $[(CH_3)_2NBH_2]_2$, $[(CH_3)_2PBH_2]_3$, and hydrogen.

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[1] P. C. Keller, *Inorg. Chem.*, **10**, 2256 (1971).

[2] G. A. Hahn and R. Schaeffer, *J. Amer. Chem. Soc.*, **86**, 1503 (1964).

[3] L. D. Schwartz and P. C. Keller, *Inorg. Chem.*, **10**, 645 (1971).

[4] D. F. Shriver, "The Manipulation of Air-Sensitive Compounds," McGraw-Hill, New York, N. Y., 1969.

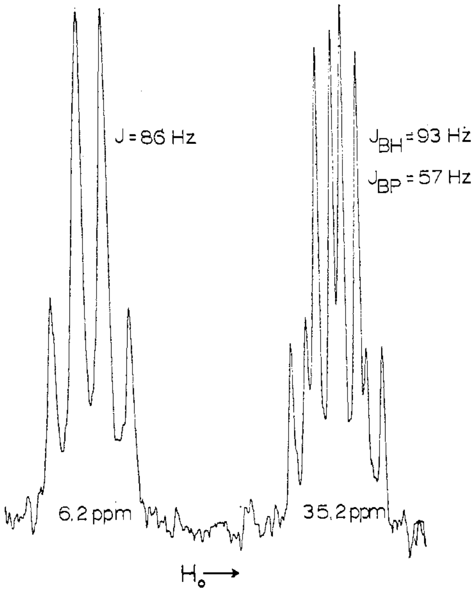

Figure 1.—Boron-11 nmr spectrum of $(CH_3)_3N–BH_2–P(CH_3)_2–BH_3$ in C_6H_6.

Characterization of $CH_3NH_2–BH_2–P(CH_3)_2–BH_3$.—Elemental analyses were as follows. *Anal.* Calcd. B, 18.5; hydridic H, 4.21; N, 11.8. Found: B, 18.1; hydridic H, 4.03; N, 11.2. The colorless crystals survive only brief exposure to air and begin to decompose slightly near the melting point giving a 60–65° melting range. They are soluble in monoglyme, acetone, and trichloroethylene but only slightly soluble in nonpolar solvents like heptane, benzene, and carbon tetrachloride and show slow solvolysis in ethanol. Boron-11 nmr (C_6H_6): quartet δ 11.1 ppm (J = 108 Hz), quartet of doublets δ 37.6 ppm (J_{BH} = 90 Hz, J_{BP} = 64 Hz); proton nmr (C_6H_6): broad singlet τ 6.12 (intensity 2), triplet τ 7.98 (J_{HNCH} = 3.0 Hz, intensity 3), doublet τ 8.95 (J_{PCH} = 5.0 Hz, intensity 6); monoisotopic mass spectrum (70 eV) [m/e (relative intensity)]: 119 (2), 118 (11), 117 (7), 116 (3), 106 (5), 105 (100), 104 (15), 103 (5), 102 (6), 90 (2), 89 (5), 88 (2), 75 (14), 74 (9), 73 (7), 72 (4), 71 (2), 70 (3), 69 (4), 68 (2), 67 (2), 66 (2), 63 (6), 62 (51), 61 (4), 60 (2), 59 (6), 58 (6), 57 (7), 56 (8), 55 (7), 54 (3), 47 (2), 46 (9), 45 (8), 44 (36), 43 (15), 42 (28), 41 (19), 40 (9), 39 (5), 32 (5), 31 (3), 30 (7), 29 (2), 28 (12), 27 (14), 26 (9); ir (KBr) in cm^{-1} (relative intensity): 3220 (vs), 3150 (m), 3010 (w), 2950 (w), 2900 (w), 2380 (sh, vs), 2350 (sh, vs), 2330 (vs), 2280 (vs), 2100 (w), 1595 (m), 1460 (m), 1420 (m), 1320 (m), 1290 (vw), 1275 (vw), 1150 (m), 1126 (s), 1080 (sh, w), 1070 (w), 1048 (m), 1002 (w), 963 (w), 941 (sh, w), 922 (s), 860 (w), 784 (vw), 752 (w), 730 (vw), 672 (vw), 640 (vw), 562 (w).

Complete pyrolysis at 240° for 15 hr produced $[CH_3NBH]_3$, $[(CH_3)_2PBH_2]_3$, and hydrogen.

Characterization of $NH_3–BH_2–P(CH_3)_2–BH_3$.—Elemental analyses were as follows. *Anal.* Calcd: B, 20.5; hydridic H, 4.80; N, 13.3; P, 29.5. Found: B, 20.8; hydridic H, 4.96; N, 11.4; P, 29.8. The colorless crystals decompose slowly on exposure to air, mp 72° dec. They are soluble in monoglyme and acetone, soluble with slow solvolysis in ethanol, methanol, and water, and slightly soluble in benzene, n-heptane, and toluene. Boron-11 nmr (C_6H_6): quartet δ 9.3 ppm (J = 100 Hz), quartet of doublets δ 36.8 ppm (J_{BH} = 88 Hz, J_{BP} = 63 Hz); proton nmr (C_6H_6): broad singlet τ 7.16 (intensity 1), doublet τ 8.94 (J_{PCH} = 5.0 Hz, intensity 2); monoisotopic mass spectrum (70 eV) [m/e (relative intensity)]: 105 (1), 104 (8), 103 (5), 102 (3), 101 (3), 100 (3), 92 (3), 91 (100), 90 (10), 89 (3), 88 (3), 87 (3), 86 (5), 85 (4), 84 (2), 83 (3), 82 (4), 75 (15), 74 (22), 73 (15), 72 (10), 70 (3), 69 (3), 68 (3), 62 (94), 61 (7), 60 (2), 59 (11), 58 (5), 57 (8), 56 (7), 55 (10), 54 (3), 48 (8), 47 (4), 46 (2), 45 (12), 44 (10), 43 (3), 42 (18), 41 (28), 40 (13), 39 (4), 38 (3), 37 (4), 30 (32), 29 (12), 28 (41), 27 (12), 26 (11); ir (KBr) in cm^{-1} (relative intensity): 3200 (s), 2960 (vw), 2910 (vw), 2330 (vs), 2290 (vs), 1575 (m), 1480 (s), 1290 (sh, w), 1280 (w), 1158 (s), 1110 (s), 1060 (s), 1020 (w), 942 (s), 922 (s), 863 (m), 758 (m), 742 (w), 712 (m), 678 (w), 628 (m), 541 (w).

Pyrolysis at 170° for 24 hr produced $B_3N_3H_6$, $(H_2NBH_2)_x$, $[(CH_3)_2PBH_2]_3$, and hydrogen.

Reaction with Boron Trifluoride.—A toluene solution of $(CH_3)_2NH–BH_2–P(CH_3)_2–BH_3$ was treated with a 10% excess of boron trifluoride for 1 hr at 25°; work-up of the mixture produced only starting materials, indicating no reaction had occurred.

Amine Exchange.—A monoglyme solution of $NH_3–BH_2–P(CH_3)_2–BH_3$ was allowed to interact with a threefold excess of trimethylamine for 40 min at 25°. Examination of the infrared spectra of the separated products revealed only the presence of unreacted starting materials.

Results and Discussion

Amine hydrochlorides react smoothly with $Li(CH_3)_2P(BH_3)_2$ according to eq 2. This process parallels the behavior of $Na(CH_3)_2N(BH_3)_2$[1] although no evidence was found for chlorination side reactions noted in the latter case.

The spectroscopic properties of the products are fully consistent with the assigned N–B–P–B chain structure. The infrared spectra compare favorably with the published data for the amine adducts of μ-$(CH_3)_2NB_2H_5$.[2] The boron-11 nmr spectra of all compounds resemble Figure 1. The high-field quartet of doublets is assigned to the terminal phosphorus-bonded BH_3 group. The low-field quartet apparently arises from a case of similar BH and BP coupling constants for the middle BH_2 group. Resolution of separate BH and BP coupling may be lost owing to line broadening resulting from interaction with the nitrogen-14 quadrupole moment. All proton nmr spectra show a strong doublet near τ 9.00 arising from the P-CH_3 protons. At lower field, N-CH_3 and NH signals appear with intensities consistent with the assigned structure. The mass spectra show no peaks at higher m/e than the parent ion.

All N–B–P–B compounds dissolve in polar aprotic solvents; with decreasing N-methyl substitution solubility in nonpolar media drops off sharply, while solubility in water, accompanied by slow hydrolysis, increases. Very slow acid hydrolysis of the di- and trimethylamine compounds may be attributed partly to solubility effects.

Burg and Sandhu[5] found that Lewis base adducts of μ-$(CH_3)_2NB_2H_5$ underwent irreversible thermal decomposition according to equation 3. The N–B–P–B

$$(\text{base})–BH_2–N(CH_3)_2–BH_3 \longrightarrow (\text{base})–BH_3 + (CH_3)_2NBH_2 \quad (3)$$

compounds pyrolyze in a similar fashion; the recovered products are $[(CH_3)_2PBH_2]_3$ and the thermal decomposition products of the appropriate amine–borane (eq 4–7). Resistance to thermal decomposition increases

$$(CH_3)_3N–BH_2–P(CH_3)_2–BH_3 \xrightarrow{240°} (CH_3)_3N\cdot BH_3 + {}^1/_3[(CH_3)_2PBH_2]_3 \quad (4)$$

$$(CH_3)_2NH–BH_2–P(CH_3)_2–BH_3 \xrightarrow[\text{slow}]{150°} H_2 + (CH_3)_2NBH_2 + {}^1/_3[(CH_3)_2PBH_2]_3 \quad (5)$$

$$CH_3NH_2–BH_2–P(CH_3)_2–BH_3 \xrightarrow{240°} 2H_2 + {}^1/_3[CH_3NBH]_3 + {}^1/_3[(CH_3)_2PBH_2]_3 \quad (6)$$

$$NH_3–BH_2–P(CH_3)_2–BH_3 \xrightarrow{170°} H_2 + B_3N_3H_6 + (H_2NBH_2)_x + [(CH_3)_2PBH_2]_3 \quad (7)$$

with increasing N-methyl substitution.

Although the resemblance between NBNB and

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[5] A. B. Burg and J. S. Sandhu, *Inorg. Chem.*, **4**, 1467 (1965).

NBPB compounds is strong in some respects, a significant difference appears in comparing reactions involving free μ-$(CH_3)_2NB_2H_5$. Burg and Sandhu found that adducts of μ-$(CH_3)_2NB_2H_5$ dissociate reversibly in the gas phase at 25° according to eq 8. For $(CH_3)_3P$,

$$\text{(base)}-BH_2-N(CH_3)_2-BH_3 \rightleftharpoons \text{base} + \mu\text{-}(CH_3)_2NB_2H_5 \quad (8)$$

$(CH_3)_3N$, and $(CH_3)_2PH$ the dissociation was estimated to be 55, 76, and 100%, respectively. The cases of the phosphine adducts are especially significant since the complexes are isomers of the NBPB compounds.

This work has produced no evidence for a dissociative process like reaction 8. Attempts to trap free base with boron trifluoride and to exchange amine bases were unsuccessful. The main cause of the inhibition of a dissociative reaction is probably severe steric strain in free μ-$(CH_3)_2PB_2H_5$. With dissociation the BPB angle must adjust to accommodate formation of a B–H–B hydrogen bridge bond. A B–P distance of 1.92 Å (found in $[(CH_3)_2PBH_2]_3$[6]) and a B···B distance of 1.93 Å (found in μ-$(CH_3)_2NB_2H_5$[7] and longer than the 1.74–1.86-Å range of hydrogen-bridged B···B distances found in boron hydrides[8]) result in an equilateral triangular PB_2 configuration and an extremely acute 60° BPB angle. Earlier attempts to prepare μ-$(CH_3)_2PB_2H_5$ from $[(CH_3)_2PBH_2]_2$[9] or from $Li(CH_3)_2P(BH_3)_2$[3] were also unsuccessful.

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[6] W. C. Hamilton, *Acta Crystallogr.*, **8**, 199 (1955).

[7] K. Hedberg and A. J. Stasick, *J. Amer. Chem. Soc.*, **74**, 954 (1952).

[8] W. N. Lipscomb, "Boron Hydrides," W. A. Benjamin, New York, N. Y., 1963.

[9] A. B. Burg and R. I. Wagner, *J. Amer. Chem. Soc.*, **75**, 3872 (1953).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, AND
THE INORGANIC MATERIALS RESEARCH DIVISION, LAWRENCE BERKELEY LABORATORY, BERKELEY, CALIFORNIA 94720

A Kinetic Study of the Intermediates in the Hydrolysis of the Hydroborate Ion

BY FRANCIS T. WANG AND WILLIAM L. JOLLY*

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The stepwise hydrolysis of hydroborate has been studied in cold 88:12 vol. % methanol–water solutions in the hydrogen ion concentration range 0.1–1.1 *M*. At −78°, BH_4^- rapidly hydrolyzes to H_2OBH_3, which, in turn, hydrolyzes to $BH_2(H_2O)_2^+$ according to the rate equation $-d \ln [H_2OBH_3]/dt = 0.0015 \text{ sec}^{-1} + 0.0016[H^+] \text{ sec}^{-1} M^{-1}$. The rate data for the hydrolysis of $BH_2(H_2O)_2^+$ solutions at −36° are consistent with the following rapid equilibrium ($K = 6.4$): $H^+ + H_2OBH_2OH \rightleftarrows BH_2(H_2O)_2^+$. The $BH_2(H_2O)_2^+$ ion is stable toward hydrolysis, whereas its conjugate base hydrolyzes to $H_2OBH(OH)_2$ according to the rate equation $-d \ln [H_2OBH_2OH]/dt = 0.017 \text{ sec}^{-1}$. At −36°, $H_2OBH(OH)_2$ hydrolyzes to $B(OH)_3$ according to the rate equation $-d \ln [H_2OBH(OH)_2]/dt = 3.3 \times 10^{-4} \text{ sec}^{-1}$. The species H_2OBH_3, $BH_2(H_2O)_2^+$, and $H_2OBH(OH)_2$ are converted to the anions BH_3OH^-, $BH_2(OH)_2^-$, and $BH(OH)_3^-$, respectively, by the addition of hydroxide. These anions undergo hydrolysis in nonbuffered, strongly alkaline solutions according to the rate equations $-d \ln [BH_3OH^-]/dt = 1.8 \times 10^{-4} \text{ sec}^{-1}$ at 20°; $-d \ln [BH_2(OH)_2^-]/dt = 2.2 \times 10^{-5} \text{ sec}^{-1}$ and $-d \ln [BH(OH)_3^-]/dt = 1.1 \times 10^{-3} \text{ sec}^{-1}$ at 0°. The boron-11 nmr spectrum of BH_3OH^- is a 1:3:3:1 quartet, with $J_{B-H} = 87$ Hz, centered 12 ppm upfield from the borate singlet.

Introduction

The hydroborate ion (otherwise known as borohydride, tetrahydroborate, and tetrahydridoborate) undergoes hydrolysis in aqueous solutions to give boric acid below pH 9 and borate above pH 9.

$$BH_4^- + H^+ + 3H_2O \longrightarrow B(OH)_3 + 4H_2$$

$$BH_4^- + 4H_2O \longrightarrow B(OH)_4^- + 4H_2$$

A variety of experimental data have shown that the hydrolysis proceeds in four steps, with the intermediate formation of trihydro-, dihydro-, and monohydroboron species.

The trihydroboron intermediate has been detected in decomposing hydroborate solutions by polarography,[1,2] by nmr,[3] and by trapping with trimethylamine.[4] In each of these studies, the solution under study was alkaline and the intermediate was probably present principally as the anion BH_3OH^-.

The dihydroboron intermediate has been prepared in essentially quantitative yields by the acid hydrolysis of hydroborate in cold (<−60°) aqueous or water–alcohol solutions.[5,6] This intermediate is relatively stable in cold acidic solutions, where it is believed to exist as $BH_2(H_2O)_2^+$, but it is unstable toward further hydrolysis is neutral solutions, where it is assumed to exist as H_2OBH_2OH.[7]

The monohydroboron intermediate has been prepared quantitatively by the reaction of diborane with water–alcohol solutions[5] at −75° and with ice[8] at −80°. The assumed formula of the product of these reactions is $H_2OBH(OH)_2$.[7] Alkaline solutions of the monohydroboron intermediate, presumably containing the ion $BH(OH)_3^-$, have been prepared by the addition of KOH to water–alcohol solutions of $BH_2(H_2O)_2^+$ and $H_2OBH(OH)_2$.[5,6]

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[1] J. A. Gardiner and J. W. Collat, *Inorg. Chem.*, **4**, 1208 (1965).

[2] J. A. Gardiner and J. W. Collat, *J. Amer. Chem. Soc.*, **87**, 1692 (1965).

[3] J. A. Gardiner and J. W. Collat, *ibid.*, **86**, 3165 (1964).

[4] R. E. Davis, E. Bromels, and C. L. Kibby, *ibid.*, **84**, 885 (1962).

[5] W. L. Jolly and T. Schmitt, *ibid.*, **88**, 4282 (1966).

[6] W. L. Jolly and T. Schmitt, *Inorg. Chem.*, **6**, 344 (1967).

[7] For water–alcohol solutions, generalized formulas such as $BH_2(OH)_x(ROH)_{2-x}^+$ and $(H_2O)_x(ROH)_{1-x}BH_2(OH)_y(OR)_{1-y}$ would be more realistic.

[8] H. G. Weiss and I. Shapiro, *J. Amer. Chem. Soc.*, **75**, 1221 (1953).