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The Hydrolysis of Octahydrotriborate in Cold Acidic Methanol-Water Solutions. The Preparation of $B_3H_7OH_2$ and $B_3H_7OH^-$.

William L. Jolly*, Janice W. Reed, and Francis T. Wang

ABSTRACT:

In methanol-water solutions of HCl at -78°, the octahydrotriborate ion reacts to form one mole of hydrogen and a solution of B_3H_7, which we formulate as $B_3H_7OH_2$. The rate of this reaction, for $[H^+] \leqslant 1.25$ M, is given by the expression $-d[B_3H_8^-]/dt = k_1[B_3H_8^-][H^+]$, where $k_1 = 2.9 \times 10^{-3}$ M^{-1} min^{-1}. When a solution of $B_3H_7OH_2$ is warmed to -45°, complete hydrolysis to boric acid and hydrogen occurs. The rate of the latter reaction, for $[H^+] \leqslant 1.5$ M, is given by the expression $-d[B_3H_7OH_2]/dt = k_2[B_3H_7OH_2]$, where $k_2 = 3.0 \times 10^{-3}$ min^{-1}. The hydroxyheptahydrotriborate ion, $B_3H_7OH^-$, is formed by the addition of hydroxide to a $B_3H_7OH_2$ solution at -78°. The anion undergoes a quantitative base-catalyzed disproportionation to borate and borohydride at temperatures above -65°: $B_3H_7OH^- + 2\ OH^- + H_2O \rightarrow 2\ BH_4^- + B(OH)_4^-$.

It is well established that the first step of the reaction of the octahydrotriborate ion, $B_3H_8^-$, with an acid such as hydrogen chloride is the formation of B_3H_7 and H_2.[1-5] Free B_3H_7 has never been isolated; generally it reacts with any Lewis base present in the reaction system to form an adduct B_3H_7L. For example, a solution of hydrogen chloride in acetonitrile reacts with $B_3H_8^-$ as follows,[5]

$$B_3H_8^- + HCl + CH_3CN \rightarrow Cl^- + H_2 + B_3H_7NCCH_3$$

The corresponding reaction in water has never been observed presumably because of rapid hydrolysis of the initially-formed $B_3H_7OH_2$. It has been reported that the rate of hydrolysis of $B_3H_8^-$ in aqueous solution is comparable to, or slightly lower than, that of the BH_4^- ion.[6] Because of previous success in studying the successive steps in the hydrolysis of the BH_4^- ion at low temperatures in aqueous 8 M HCl and in acidic water/alcohol solutions,[7-9] we decided to apply similar techniques in this study of the hydrolysis of $B_3H_8^-$.

Experimental Section

Potassium Octahydrotriborate. - Sodium octahydrotriborate was prepared by literature procedures[10,11] and was converted to the trisdioxane complex. A nearly saturated aqueous solution of the crude trisdioxane complex was mixed with concentrated KOH solution to precipitate the potassium salt. This precipitate was dissolved in tetrahydrofuran; the solution was filtered to remove KOH and insoluble salts, and then the dioxane complex was precipitated by the addition of dioxane. An aqueous solution of this complex was evaporated to dryness, and the product was dried in vacuo at 100°. Analysis by measurement of the hydrogen released upon acid hydrolysis indicated a purity of 99.7%, and potassium analysis (by precipitation of potassium tetraphenylborate) indicated a purity of 99.4%.

Kinetic Studies. - A fragile bulb containing 0.5-2 mmol of KB_3H_8 dissolved in 2 ml of 88% methanol/12% water was lowered into a reaction vessel[12] containing a known amount of HCl dissolved in 30 ml of the same solvent. After thoroughly cooling the reaction vessel to -78° in a dry-ice bath, the system (which included a manometer) was evacuated and then closed off. The reaction was started by breaking the fragile bulb, and the pressure was measured as a function of time. In the case of the relatively fast reactions, the reaction was followed to completion and the total evolved hydrogen was measured by Toepler-pumping it through a liquid nitrogen-cooled trap into a gas buret. In some runs, after hydrogen evolution had ceased at -78°, the -78° bath was replaced with a -45° chlorobenzene slush and the further evolution of hydrogen was followed manometrically.

$B_3H_7OH^-$. - A fragile bulb containing 1 mmol of KB_3H_8 in 2 ml of 88% methanol/12% water was lowered into a reaction vessel[12] containing 3 ml of the same solvent, 2 M in HCl. The vessel was cooled to -78° and then evacuated. The fragile bulb was broken; the reaction was alloweed to proceed for 30 hours, and then 35 ml of 0.5 M NaOH (in 88% methanol/12% water), cooled to -78°, was added. For the reactions designed to determine whether hydrogen was evolved upon addition of OH^-, an apparatus with two fragile bulbs was used.[12]

NMR. - The boron-11 nmr spectra were recorded at 57.78 MHz with a spectrometer which included a Bruker 42 kilogauss superconducting magnet and Nicolet 1180 data system. For the low temperature studies, the cold solutions were pipetted with a dry ice-jacketed pipet and transferred to cooled 10-mm quartz nmr tubes. The tubes were stored in a dry-ice bath until ready to be placed in the spectrometer.

Results and Discussion

Acidic Solutions. The stoichiometry of the solvolysis of $B_3H_8^-$ was studied at -78° in 88% methanol/12% water containing hydrogen chloride in the concentration range 0.20-8 *M*. The total amount of hydrogen evolved was measured after the reaction rate became negligible or was extrapolated from kinetic data obtained during approximately the first 80% of reaction. The data given in Table I indicate that one mole of hydrogen is formed per mole of $B_3H_8^-$. We assume that, in the reaction, a proton abstracts a hydride ion from the $B_3H_8^-$ ion to form B_3H_7, which then exists in the methanol-water solution as a solvate analogous to the well-known B_3H_7-Lewis base adducts B_3H_7L.[1,3-5] For simplicity, we represent the solvated B_3H_7 as a hydrate, although it is probably in equilibrium with a considerable amount of methanolate.

$$B_3H_8^- + H^+ + H_2O \xrightarrow[-78°]{k_1} B_3H_7OH_2 + H_2 \qquad (1)$$

We studied the rate of reaction 1 at various hydrogen ion concentrations in the range 0.25-1.25 *M*. The data indicate that the reaction is first-order in $B_3H_8^-$. Thus for the case of the run with 1.25 M HCl, during which the hydrogen ion concentration underwent a negligible change, a semilogarithmic plot of $P_\infty - P$ versus time (shown in Figure 1) is linear. The calculated pseudo-first-order rate constants, k_1', corresponding to various H^+ and $B_3H_8^-$ concentrations are listed in Table II. A plot of k_1' versus hydrogen ion concentration (see Figure 2) is linear with a zero intercept at $[H^+] = 0$ and indicates the following rate law for reaction 1, with $k_1 = 2.88 \times 10^{-3}$ $\underline{M}^{-1}$ min^{-1}.

$$-\frac{d[B_3H_8^-]}{dt} = k_1[B_3H_8^-][H^+] \qquad (2)$$

Thus, the hydrolysis of the octahydrotriborate ion in 88% methanol/12% water solutions where $[H^+] \leqslant 1.25$ M at -78° is first-order in both octahydrotriborate ion and hydrogen ion. An attempt to study the kinetics of the reaction in solutions maintained at constant ionic strength by the addition of lithium chloride was unsuccessful because of the LiCl-catalyzed reaction of HCl with methanol to form methyl chloride.

From the value of k_1 determined in the 0.25-1.25 M HCl solutions at -78°, one calculates that reaction 1 should have a half-life of 80 minutes in 3 M HCl and a half-life of 60 minutes in 4 M HCl. However, we found the rate of reaction under these conditions to be too fast to measure accurately; the half-life was approximately two minutes in 3 M HCl and less than one minute in 4 M HCl. We suspect that this disproportionate increase in reaction rate in the more concentrated HCl solutions is due to extreme nonideality of the solutions, i.e. to a nonlinear relation between the activity and the concentration of the hydrogen ion.

When $B_3H_7OH_2$ solutions were warmed to -45°, complete hydrolysis to boric acid was observed:

$$B_3H_7OH_2 + 8\ H_2O \xrightarrow[-45°]{k_2} 3\ B(OH)_3 + 8\ H_2 \qquad (3)$$

We studied the rate of reaction 3 at -45° as a function of hydrogen ion concentration in the range 0.25-8 $\underline{M}$ H^+ by the same techniques used in studying reaction 1 at -78°. Semilogarithmic plots of $P_\infty - P$ vs time for the runs in which $[H^+] \leqslant 3\ \underline{M}$ are linear, as shown in Figure 3 for the run at 1.5 $\underline{M}$ H^+. Thus reaction 3 is first-order with respect to the concentration of $B_3H_7OH_2$ in $[H^+] \leqslant 3\ \underline{M}$. Values of the first-order rate constant k_2 were obtained from a least-squares treatment of the kinetic data and are listed as a function of hydrogen ion concentration in Table III. The data show that the rate of reaction 3 is independent of hydrogen ion concentration at $[H^+] \leqslant 1.5\ \underline{M}$ but that the reaction is acid-catalyzed in the more acidic solutions. Semilogarithmic plots of $P_\infty - P$ vs time for the data obtained in 3.5, 4, and 8 $\underline{M}$ HCl at -45° are not linear. We attempted to interpret the rate data in these runs in terms of a second-order dependence on $B_3H_7OH_2$; indeed we found that $1/(P_\infty - P)$ is a linear function of time for the 4 and 8 $\underline{M}$ HCl rate data but is non-linear for the 3.5 $\underline{M}$ HCl data. The results suggest that the rate law for reaction 3 may be of the type given by Eq. 4.

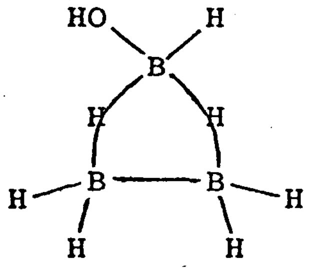
$$\frac{-d[B_3H_7OH_2]}{dt} = k_2[B_3H_7OH_2] + k_3[B_3H_7OH_2]^2[H^+] \qquad (4)$$

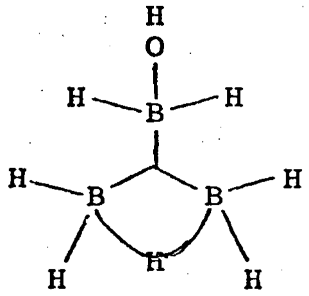
However, attempts to fit the data to this rate law were only qualitatively successful. Indeed, attempts to rationalize the rate data in the more concentrated acid solutions are probably not justifiable in the absence of quantitative information regarding the effective hydrogen ion activity in these solutions. Probably the most we can now say is that, on going to high HCl concentrations in 88% methanol/12% water, the hydrolysis of $B_3H_7OH_2$ accelerates (acid catalysis) and probably becomes greater than first order in $B_3H_7OH_2$.

The ^{11}B nmr spectrum of a solution of $B_3H_7OH_2$ at -78° consists of a very broad peak (26 ppm upfield of external methyl borate) which becomes narrower at -45°. The peak is asymmetric, with a shoulder on the high field side, as in the spectra reported for $B_3H_7O(C_2H_5)_2$ and $B_3H_7 \cdot THF$.[13] Thus the spectrum is consistent with a structure for $B_3H_7OH_2$ in which there are two different types of boron atoms, in a 2:1 ratio.

Alkaline Solutions. Because BH_3OH_2 can be deprotonated by strong base to form BH_3OH^-, we assume that $B_3H_7OH_2$ could likewise be deprotonated to form $B_3H_7OH^-$. We added excess base to a solution containing $B_3H_7OH_2$ at -78° and observed no hydrogen evolution due to hydrolysis even when the solution was warmed to room temperature. This behavior suggests that the $B_3H_7OH_2$ reacted to form a new species, because even at -45° $B_3H_7OH_2$ undergoes hydrolysis. The boron-11 nmr spectrum of the initially formed alkaline solution at -78° showed two broad peaks with an intensity ratio of 1:2 centered ~10.1 ppm downfield and ~39.2 ppm upfield, respectively, from a weak peak due to a trace of borate present. The spectrum remained unchanged up to -65°, and a spectrum recorded at -65° is shown in Figure 4. Under high resolution, the borate signal was found to be split into two or more peaks that we attribute to the hydroxymethoxyborate species, $B(OH)_{4-n}(OCH_3)_n^-$, that are expected to exist in methanol/water solutions of borate. As confirmation of this interpretation of the splitting, we observed that the spectrum of an alkaline aqueous solution of borate consists of one sharp peak and that, upon addition of methanol to the solution, the signal is split.

Presumably the hydroxyl group is attached to only one of the three boron atoms of B_3H_7. Hence the two broad peaks at -10.1 and +39.2 ppm can be assigned to the two different types of boron in $B_3H_7OH^-$, assuming a structure such as one of the following.[14]





Probably all the non-hydroxyl hydrogen atoms of the ion undergo exchange in a period shorter than the nmr time scale, just as in the case of the $B_3H_8^-$ ion.[15] Two peaks were observed by Dolan et al[5] in the ^{11}B spectra of the analogous species, $B_3H_7NCCH_3$ and $B_3H_7OCHN(CH_3)_2$; however, in contrast to our observations for $B_3H_7OH^-$, they found that the weaker peaks were upfield from the stronger peaks. This difference between $B_3H_7OH^-$ and the neutral

B_3H_7 adducts is probably related in cause to the fact that the ^{11}B signal of the hydroxyborohydride ion is at lower field than that of amine borane.[9,16]

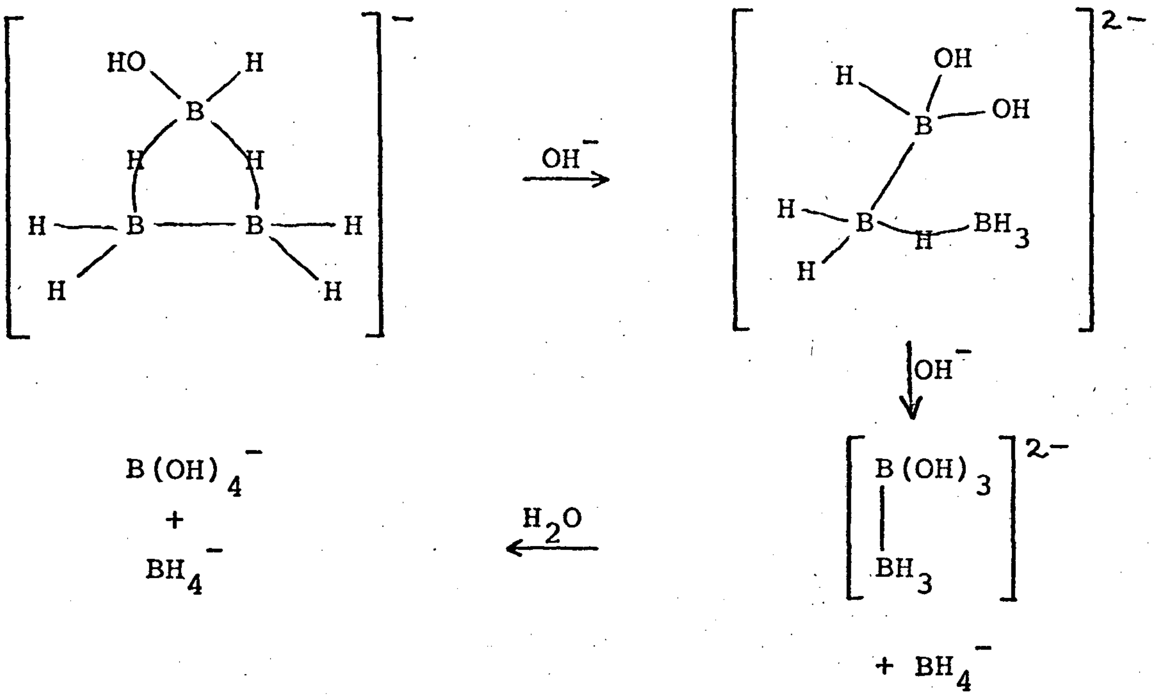
When solutions containing $B_3H_7OH^-$ were warmed above -65°, it was apparent from changes in the nmr spectra that the $B_3H_7OH^-$ decomposed to give borate and borohydride. Figure 6 shows a series of spectra recorded approximately two minutes, one-half hour, two hours, and three hours after warming the sample to -28°. It can be seen that, as the signals due to $B_3H_7OH^-$ disappeared, the signal at 0 ppm due to $B(OH)_{4-x}(OCH_3)_x^-$ and the quintet at 45 ppm due to borohydride grew in. (The very broad background signal was due to the boron present in the Pyrex probe insert.) Thus one may write the decomposition reaction as follows.

$$B_3H_7OH^- + 2\ OH^- + H_2O \rightarrow 2\ BH_4^- + B(OH)_4^- \qquad (5)$$

In writing equation 5 we have ignored the presence of methanol in the solvent to simplify the formulation of the species. To verify the stoichiometry we integrated the signals in the spectra of Figure 5. On going from spectrum (a) to spectrum (c), the increase in the $B(OH)_{4-x}(OCH_3)_x^-$ signal area is 1.07 times the decrease in the low-field $B_3H_7OH^-$ signal area. This ratio is, within experimental error, consistent with the formation of one mole of borate for each mole of $B_3H_7OH^-$ decomposed, as required by equation 5. In spectrum (d), the ratio of the BH_4^- signal area to the $B(OH)_{4-x}(OCH_3)_x^-$ signal area was determined, after empirical correction for the relatively long relaxation time of BH_4^-, to be 2.06. This result is also consistent with equation 5.

Semiquantitative experiments showed that the decomposition of $B_3H_7OH^-$ to borate and borohydride is based catalyzed. For example, using ^{11}B nmr as an analytical probe, solutions of $B_3H_7OH^-$ were studied at 0°. A solution 0.4 M in OH^- underwent about 90% decomposition in five minutes; a solution 1 M in OH^- underwent about 95% decomposition in five minutes, and a solution 2 M in OH^- underwent more than 98% decomposition in less than five minute Because $B_3H_7OH^-$ is undoubtedly an intermediate in the hydrolysis of hot aqueous alkaline solutions of $B_3H_8^-$, these results indicate that borohydride should be an important product of this hydrolysis. Indeed, we found that after heating a solution of $B_3H_8^-$ in 15 M NaOH at 80° for one hour, the nmr spectrum showed no trace of $B_3H_8^-$, but showed the presence of BH_4^- and $B(OH)_4^-$ in the ratio 0.7:1, respectively. A study of the kinetics of the hydrolysis of $B_3H_8^-$ in alkaline solutions would be very interesting.

It is tempting to speculate on the mechanism of the decomposition of $B_3H_7OH^-$. A mechanism based on successive attack of hydroxide ions on the most positive boron atom in the group, as shown in the following scheme, seems reasonable.


OH⁻
OH⁻
H2O
B(OH)4⁻
+
BH4⁻
B(OH)3
BH3
2−
+ BH4⁻

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References and Notes

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(12) The apparatus was similar to that illustrated in ref. 9.

(13) G. Kodama, Inorg. Chem., 14, 452 (1975).

(14) Other structures can be derived from either of these structures by interchanging the hydroxyl group with any one of the terminal hydrogen atoms. Even though some of the derived structures would have three different boron atoms, they are consistent with the ^{11}B nmr spectrum if we assume that the ion is rapidly fluxional with respect to the non-hydroxyl hydrogen atoms.

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(16) R. Schaeffer, in "Progress in Boron Chemistry," Vol. 1, H. Steinberg and A. L. McCloskey, Pergamon Press, Oxford, 1964, pp. 417-462.

Table I. Hydrogen Produced per Mole of $B_3H_8^-$ at -78° in 88% Methanol Solutions as a Function of Hydrogen Ion Concentration.

$[H^+]$, $\underline{M}$	$B_3H_8^-$, mmol	$H_2/B_3H_8^-$
0.25	2.01	0.97
1.00	1.10	1.03
1.25	1.00	0.99
1.50	1.02	1.03
2.95	0.70	1.04
4.02	0.97	1.03
8.03	1.02	1.08

Table II. Effect of Acid Concentration on the Pseudo-First-Order Rate Constant for the Solvolysis of $B_3H_8^-$ at -78°

$[H^+]$, M	$B_3H_8^-$, M	k_1', $min^{-1} \times 10^3$
0.25	0.06	0.42[a]
0.60	0.032	1.81
1.00	0.034	2.90
1.25	0.031	3.60

[a] Reaction not "flooded" with H^+. Constant calculated assuming first order in both $B_3H_8^-$ and H^+, using integrated form of rate law.

Table III. The Rate Constant k_2 as a Function of $[H^+]$ for the Hydrolysis of $B_3H_7OH_2$ at -45°.

H^+, M	k_2, $min^{-1} \times 10^3$
0.25	2.72
1.00	3.22
1.25	3.28
1.50	2.94
3.00	7.01

Figure Captions

Figure 1. Semilogarithmic plot of $P_\infty - P$ vs time for the hydrolysis of KB_3H_8 in 88% methanol/12% water at -78°, with 1.25 $\underline{M}$ HCl.

Figure 2. Plot of pseudo-first-order rate constant k_1' vs hydrogen ion concentration, for hydrolysis of KB_3H_8 in 88% methanol/12% water at -78°.

Figure 3. Semilogarithmic plot of $P_\infty - P$ vs time for the hydrolysis of $B_3H_7OH_2$ in 88% methanol/12% water at -45°, with 1.25 $\underline{M}$ HCl.

Figure 4. Boron-11 nmr spectrum of $B_3H_7OH^-$ in 88% methanol/12% water at -65°.

Figure 5. Boron-11 nmr spectra of decomposing $B_3H_7OH^-$ solution. (a) After 2 min; (b) after 30 min; (c) after 2 hr; (d) after 3 hr.

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