Contribution from the Department of Chemistry, University of California,
and the Materials and Molecular Research Division, Lawrence Berkeley Laboratory, Berkeley, California 94720

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

WILLIAM L. JOLLY,* JANICE W. REED, and FRANCIS T. WANG

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In methanol–water solutions of HCl at −78 °C, the octahydrotriborate ion reacts to form 1 mol of hydrogen and a solution of B_3H_7, which we formulate as $B_3H_7OH_2$. The rate of this reaction, for $[H^+] \leq 1.25$ 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 °C, complete hydrolysis to boric acid and hydrogen occurs. The rate of the latter reaction, for $[H^+] \leq 1.5$ 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 °C. The anion undergoes a quantitative base-catalyzed disproportionation to borate and borohydride at temperatures above −65 °C: $B_3H_7OH^- + 2OH^- + H_2O \rightarrow 2BH_4^- + B(OH)_4^-$.

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 tris(dioxane) complex. A nearly saturated aqueous solution of the crude tris(dioxane) 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 °C. 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 the reaction vessel was thoroughly cooled to −78 °C 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 °C, the −78 °C bath was replaced with a −45 °C 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 °C and then evacuated. The fragile bulb was broken; the reaction was allowed to proceed for 30 h, and then 35 mL of 0.5 M NaOH (in 88% methanol–12% water), cooled to −78 °C, 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]

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

$[H^+]$, M	amt of $B_3H_8^-$, mmol	$H_2:B_3H_8^-$	$[H^+]$, M	amt of $B_3H_8^-$, mmol	$H_2:B_3H_8^-$
0.25	2.01	0.97	2.95	0.70	1.04
1.00	1.10	1.03	4.02	0.97	1.03
1.25	1.00	0.99	8.03	1.02	1.08
1.50	1.02	1.03			

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

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

NMR. The boron-11 NMR spectra were recorded at 57.78 MHz with a spectrometer which included a Bruker 42-kG superconducting magnet and a 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 °C 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 1 mol of hydrogen is formed/mol 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.

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

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 $P_\infty - P$ vs. time (shown in Figure 1) is linear. The calculated pseudo-first-order rate constants, k_1', corre-

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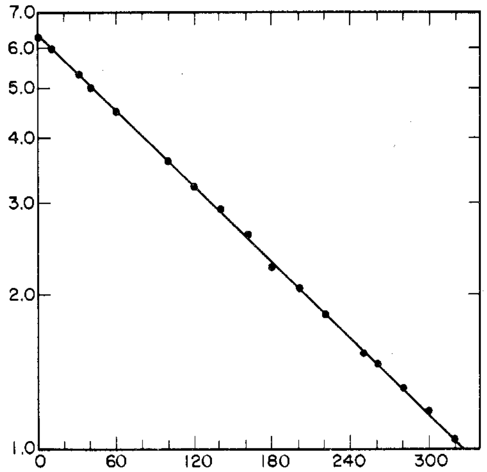


Figure 1. Semilogarithmic plot of $P_\infty - P$ vs. time for the hydrolysis of KB_3H_8 in 88% methanol–12% water at −78 °C, with 1.25 M HCl.

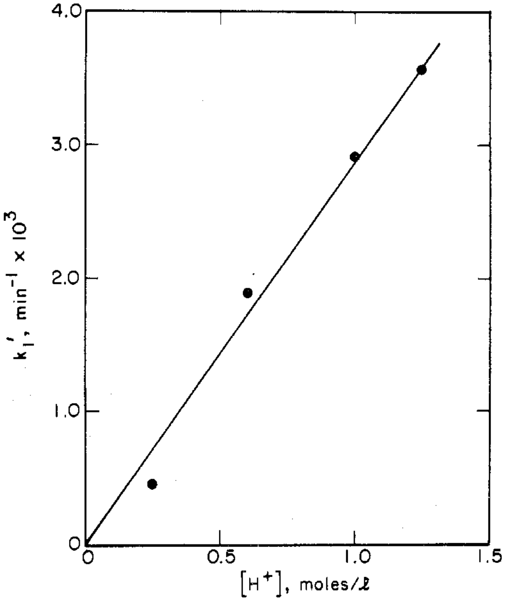


Figure 2. Plot of pseudo-first-order rate constant k_1' vs. hydrogen ion concentration, for hydrolysis of KB_3H_8 in 88% methanol–12% water at −78 °C.

sponding to various H^+ and $B_3H_8^-$ concentrations are listed in Table II. A plot of k_1' vs. 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 $k_1 = 2.88 \times 10^{-3}$ M^{-1} min^{-1}.

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

Thus, the hydrolysis of the octahydrotriborate ion in 88% methanol–12% water solutions where $[H^+] \leq 1.25$ M at −78 °C 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 °C, one calculates that reaction 1 should have a half-life of 80 min in 3 M HCl and a half-life of 60 min 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 2 min in 3 M HCl and less than 1 min 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.

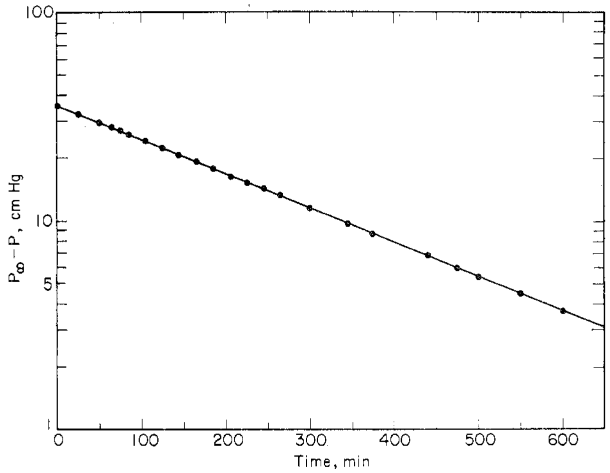


Figure 3. Semilogarithmic plot of $P_\infty - P$ vs. time for the hydrolysis of $B_3H_7OH_2$ in 88% methanol–12% water at −45 °C, with 1.25 M HCl.

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

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

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

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

We studied the rate of reaction 3 at −45 °C as a function of hydrogen ion concentration in the range 0.25–8 M H^+ by the same techniques used in studying reaction 1 at −78 °C. Semilogarithmic plots of $P_\infty - P$ vs. time for the runs in which $[H^+] \leq 3$ M are linear, as shown in Figure 3 for the run at 1.5 M H^+. Thus reaction 3 is first order with respect to the concentration of $B_3H_7OH_2$ in $[H^+] \leq 3$ 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 $[H^+] \leq 1.5$ 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 M HCl at −45 °C 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 M HCl rate data but is nonlinear for the 3.5 M HCl data. The results suggest that the rate law for reaction 3 may be of the type given by eq 4.

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

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

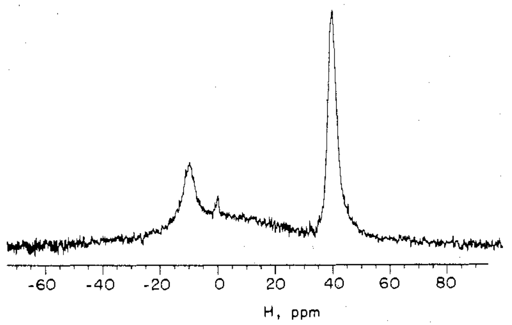


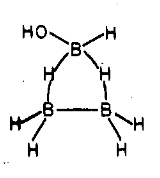
Figure 4. Boron-11 NMR spectrum of $B_3H_7OH^-$ in 88% methanol–12% water at −65 °C.

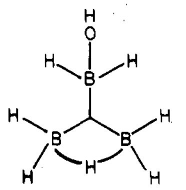
becomes greater than first order in $B_3H_7OH_2$.

The ^{11}B NMR spectrum of a solution of $B_3H_7OH_2$ at −78 °C consists of a very broad peak (26 ppm upfield of external methyl borate) which becomes narrower at −45 °C. 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 assumed 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 °C 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 °C $B_3H_7OH_2$ undergoes hydrolysis. The boron-11 NMR spectrum of the initially formed alkaline solution at −78 °C 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 °C, and a spectrum recorded at −65 °C 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, $B(OH)_{4-x}(OCH_3)_x^-$, 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 nonhydroxyl 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]

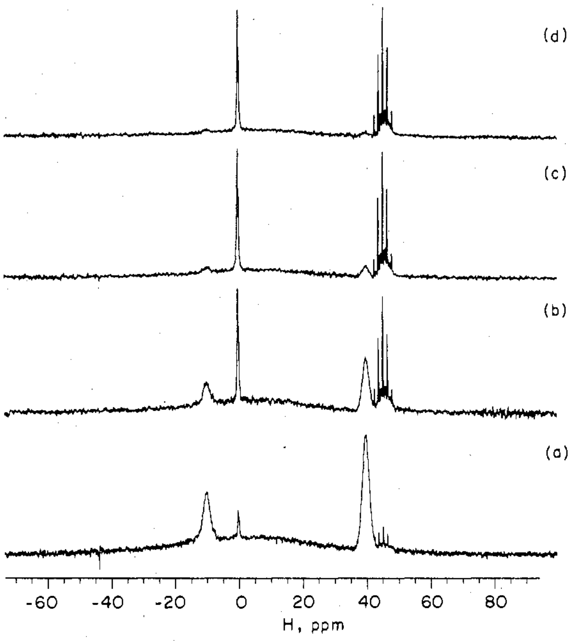


Figure 5. Boron-11 NMR spectra of decomposing $B_3H_7OH^-$ solution: (a) after 2 min; (b) after 30 min; (c) after 2 h; (d) after 3 h.

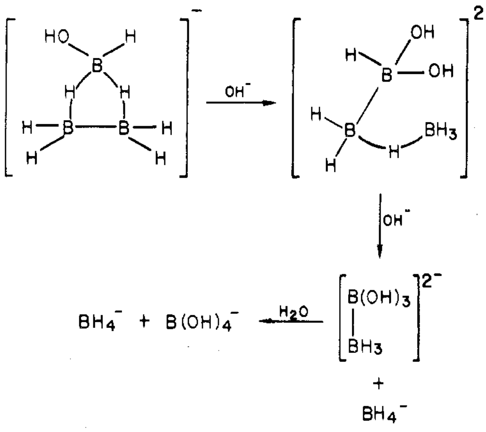
When solutions containing $B_3H_7OH^-$ were warmed above −65 °C, it was apparent from changes in the NMR spectra that the $B_3H_7OH^-$ decomposed to give borate and borohydride. Figure 5 shows a series of spectra recorded approximately 2 min, $^1/_2$ h, 2 h, and 3 h after warming of the sample to −28 °C. 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

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

In writing eq 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 1 mol of borate for each mole of $B_3H_7OH^-$ decomposed, as required by eq 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 eq 5.

Semiquantitative experiments showed that the decomposition of $B_3H_7OH^-$ to borate and borohydride is base catalyzed. For example, by use of ^{11}B NMR as an analytical probe, solutions of $B_3H_7OH^-$ were studied at 0 °C. A solution 0.4 M in OH^- underwent about 90% decomposition in 5 min; a solution 1 M in OH^- underwent about 95% decomposition in 5 min, and a solution 2 M in OH^- underwent more than 98% decomposition in less than 5 min. 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 °C for 1 h, 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.

Scheme I



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 Scheme I, seems reasonable.

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Registry No. $B_3H_8^-$, 12429-74-2; $B_3H_7OH_2$, 60718-92-5; $B_3H_7OH^-$, 68438-59-5.

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Contribution from the Institute of Inorganic Chemistry,
Free University Berlin, D-1000 Berlin 33, West Germany

Studies of the Interactions between Boron Trihalides and Tris(ethylthio)borane with Hydrogen Sulfide and Their Reactions with Tetraalkylammonium Hydrosulfides

GERT HELLER* and WOLFGANG EYSENBACH[1]

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Thiohydrolysis in the $BX_3/H_2S/NR_4SH$ system, where X = Cl, Br, or SC_2H_5 and R = CH_3 or C_2H_5, has been investigated; the BX_3/H_2S system was considered as a comparative standard. At 195 K the $BCl_3/H_2S/NR_4SH$ and $BBr_3/H_2S/NR_4SH$ systems always lead to the formation of the thioloborates $NR_4[BCl_3SH]$ and $NR_4[BBr_3SH]$, respectively. No thiohydrolysis occurred in these systems, which is in contrast to the $B(SC_2H_5)_3/H_2S/NR_4SH$ system. At 195 K in liquid H_2S, $B(SC_2H_5)_3$ and NR_4SH in up to 2:1 molar ratio reacted to yield the thioborates $(NR_4)_{2-x}[B_3S_3(SH)_{4-y}(SR)_{y+1-x}]$, where $x = 0$ or 1 and $y = 0$, 1, or 2. The Raman spectrum of the adduct $H_2S{\cdot}BCl_3$ at 195 K was recorded. BBr_3 reacts in liquid H_2S at 195 K to yield $BBr(SH)_2$ which, at elevated temperatures, is converted to $(-BBr-S-)_3$ with the evolution of H_2S.

Introduction

Interactions in the system $BX_3/H_2S/NR_4SH$ (X = Cl, Br, or SC_2H_5; R = CH_3 or C_2H_5) have been studied in order to elucidate whether or not it is possible for BX_3 to react under displacement of X^- by HS^- or S^{2-} ions and formation of thioborates. So far, compounds of the latter type have been prepared either by solid-state or solid/gas reactions at high temperatures, e.g., by reaction of B_2S_3 with metal sulfides,[2] by reaction of elemental boron with an alkali metal sulfide and a mixture of H_2S and H_2,[3] or by reaction of $LiBH_4$ with elemental sulfur. By carrying out the last reaction in ether, the addition product, the thioloborate $Li[BH_3SH]$, was obtained.[4] In contrast to thioborates, thioloborates are accessible from liquid H_2S at 195 K according to the equation $NR_4SH + BX_3 \rightleftharpoons NR_4[BX_3SH]$.[5]

Tris(alkylthio)boranes have been prepared by the reaction of boron trihalides with an excess of alkanethiol.[6] Experiments failed, however, to produce thioborates by reacting the former with H_2S and an alkali metal thiolate in either methyl- or ethylthiol in a high-vacuum apparatus.

An important factor for the understanding of the chemistry of $BX_3/H_2S/NR_4SH$ systems is the knowledge of the corresponding BX_3/H_2S system. There is indeed much known about these systems;[6–9] however, it is not clear, what products of BBr_3 or $B(SR)_3$ are present in H_2S at 195 K.

Experimental Section

Apparatus. The utilized high-vacuum apparatus consisted of three major segments: the pump stand, the vacuum line, and the assembly for cleaning the N_2. The pump stand essentially consisted of a Hg diffusion pump, connected in series with a turning slide pump, and a shortened McLeod manometer, which was situated between two cooling traps.

The main vacuum line was connected to the pump stand by a stopcock with a 12-mm bore. To this were attached 3-L or 6-L gas containers and the assembly for cleaning the N_2 and a small modified Stock-type apparatus with a Hg manometer for the distillation of gases and—when needed—reaction bulbs and Schlenk tubes and similar reaction vessels connected by four separate entry or exit ports. The main vacuum line and the gas containers were protected against

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