Title
STUDIES OF THE HYDROXYBOROHYDRIDE AND TRIBOROHYDRIDE IONS

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Contents

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Abstract

Employing a quenching flow reactor, we have prepared large quantities of alkaline solutions containing two different compounds in high yield, sodium hydroxytrihydroborate and sodium peroxynitrite. The percent yield of the hydroxyborohydride ion and the peroxynitrite ion is dependent on the reaction time as well as the concentration of the starting reagents.

Compounds containing functional groups not reduced by or sluggishly reduced by the borohydride ion were treated with the hydroxyborohydride ion, BH_3OH^-, to evaluate the latter as a reducing agent and to allow comparison of its reducing power with that of the borohydride ion. In aqueous solution at pH 11.9 and 0°, ethyl benzoate was reduced to benzyl alcohol in 89% yield. Benzonitrile was reduced to benzylamine at pH 12.5 and 25° in 89% yield. Nitrobenzene was reduced to aniline at pH 11.7 and 6° in 78% yield. The following ketones were reduced by BH_3OH^- to alcohols in greater than 70% yield: benzophenone, cyclopentanone, cyclohexanone, 2-methylcyclohexanone, d-camphor, and 4-tert-butylcyclophexanone. Octyl chloride and benzhydril choloride were not reduced by BH_3OH^-.

The hydrolysis of the octahydrotriborate ("triborohydride") ion has been studied in cold methanol-water-hydrochloric acid solutions in which the methanol concentration ranged from 0 to

88 percent by volume and the hydrogen ion concentration ranged from 0.25 to 8 M. At -78°, in 88% methanol solutions (0.25 to 8M H^+), one mole of hydrogen is evolved per mole of $B_3H_8^-$, indicating the formation of $B_3H_7OH_2$. However in 8 M HCl solutions with 0 to 70% methanol, 4.5 moles of hydrogen per $B_3H_8^-$ were obtained at -78°. Upon warming any of the solutions to room temperature, complete hydrolysis took place, giving additional hydrogen to make a total of 9 moles of hydrogen per mole of $B_3H_8^-$.

The $B_3H_7OH_2$ was converted to $B_3H_7OH^-$ by the addition of hydroxide. However, $B_3H_7OH^-$ was found to be unstable, decomposing to give BH_4^- and $B(OH)_4^-$ at temperatures above -41°. In strong base (2 to 16 M OH^-), and at elevated temperatures, $B_3H_8^-$ solutions also decompose to hydrogen, BH_4^- and $B(OH)_4^-$. The boron-11 nmr spectrum of $B_3H_7OH^-$ consists of two bands with an intensity ratio of 1:2, centered 10.22 ppm downfield and 39.29 ppm upfield from the borate signal, respectively.

PART 1-A: CHEMICAL SYNTHESES WITH A QUENCHED FLOW REACTOR. HYDROXYTRIHYDROBORATE AND PEROXYNITRITE.*

Abstract

Employing a quenching flow reactor, we have prepared large quantities of alkaline solutions containing two different compounds in high yield, sodium hydroxytrihydroborate and sodium peroxynitrite. The percent yield of the hydroxyborohydride ion and the peroxynitrite ion is dependent on the reaction time as well as the concentration of the starting reagents.

Introduction

The technique of mixing two streams of reactant solutions in a reaction tube with downstream injection of a solution containing a quenching reagent has been used for studying the kinetics of fast reactions but does not seem to have been applied to laboratory synthesis. The method is ideal for a synthesis involving the formation of an intermediate species which (1) must be prepared under conditions such that its half-life is in the range between a millisecond and several seconds and (2) can be stabilized by rapid reaction with a quenching reagent. We now report the successful use of this method for preparing solutions of two different compounds in high yield, sodium hydroxytrihydroborate and sodium peroxynitrite.

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*This work by J.W. Reed, H. H. Ho, and W. L. Jolly was published in J. Am. Chem. Soc. 96, 1248 (1974).

Experimental

Materials. The $NaBH_4$ (Alfa), HCl (J. T. Baker) and NaOH (Mallinckrodt) used to prepare the BH_3OH^- solutions were reagent grade and used as purchased.

Synthesis. The apparatus consists of a Lucite rod bored to a depth of 10 cm with a 3-mm hole. Two 1.5-mm holes for the introduction of the reactants enter from the side of the rod, joining the 3-mm tube tangentially at its inner end. A third 1.5-mm hole, for the quenching solution, enters the tube at a point 5 cm from the two reactant holes. The holes are connected to glass tubes on the outside of the rod; these are connected through glass and Teflon needle valves to siphon tubes inserted into three separate bottles. The bottles can be simultaneously pressurized with nitrogen gas at a regulated pressure from a cylinder. Before each run, the needle valves are adjusted so that the flow rates of the three solutions are equal. The reaction tube is mounted vertically, and the quenched product is collected in a beaker placed beneath the open end of the tube.

Precipitation Attempts. In all the precipitation attempts cold, 0^o, solutions containing the cations were mixed (first on test tube scale, later on a large scale if seemed promising) with BH_3OH^- solutions at 0^o. The mixtures were maintained at 0^o for at least 3 hours and if precipitation occurred, the precipitate was filtered, dried and analyzed for hydrogen and boron.

Kinetic Studies. The apparatus for the kinetic study was similar to that of Figure 1, only the small 5 ml bulb was replaced with a 100-ml round-bottomed flask. Ninety ml of NaOH solution of the desired concentration, along with sufficient NaCl to make the final ionic strength 0.35 M, was added to the round-bottomed flask and allowed to equilibrate in the thermostated bath ($\pm0.1^{o}$). Approximately 2 ml of cold (0^{o}) BH_3OH^- solution was added to the round bottomed flask which was then connected to a gas buret by way of a 19/38 joint. After the entire system had equilibrated, stopcock C was closed to the air, the timer was turned on and a zero volume in the gas buret recorded. The rate of H_2 evolution was then followed as a function of time by monitoring the change in volume of H_2O in the buret. At the end of each run the ionic strength was verified with ion exchange.

Results and Discussion

Wang and Jolly[2] have shown that, in methanol - water solution at -78^{o}, the borohydride ion reacts very rapidly with strong acid to form H_2OBH_3. This species hydrolyzes under these conditions with a half-life of about 300 sec, but it can be deprotonated to form the relatively stable BH_3OH^- ion, which has a half-life of several hours at room temperature. An estimated effective activation energy for the H_2OBH_3 hydrolysis of 12 kcal/mol[3] corresponds to half-life about 20 msec at 0^{o}. Thus, it seemed reasonable to attempt the synthesis of BH_3OH^- using the quenched flow reactor with aqueous solutions initially at 0^{o} and with a reaction time (time between the initial mixing of H^+ and BH_4^- and the quenching with OH^-) of the order of 20 msec or less. Our experimental data are given in Table I. The change in the percentage yield of BH_3OH^- with change in reaction time was qualitatively as expected. Relatively high yields, essentially independent of reaction time, were obtained for reaction times of 10-21 msec; the yield dropped off for a reaction time of 26 msec. The decrease in the percentage yield with increasing concentration of the solutions may be due to the corresponding increase in the reaction temperature caused by the increased heat of reaction. Evidence for the BH_3OH^- ion was obtained from the boron-11 nmr spectrum of the most concentrated solutions. The spectrum consisted of a 1:3:3:1 quartet centered 13.5 ppm upfield from the borate singlet, with a B-H coupling constant of 92 Hz. The spectrum obtained is in excellent agreement with those recorded by previous workers.[2,4b]

Unsuccessful attempts were made to precipitate the BH_3OH^- ion out of solution. Very concentrated or saturated solutions containing the cations Cs^+, Ag^+, $(\phi)_3CH_3P^+$, $(\phi)_4As^+$, $(\phi)_4P^+$, Tl^+, $(\phi_3P)_2N^+$ and $C_6H_5CH_2(\phi)_3P^+$ were employed. The inability to precipitate the BH_3OH^- ion was probably due to that fact that it is not a discrete ion in solution, but is instead hydrogen bonded to the water in the system.

Kinetic study. In kinetic studies by Gardiner and Collat[4(a),(c)] and Wang and Jolly,[2] the hydrolysis of the BH_3OH^- ion was found to be acid catalyzed. Our kinetic study was limited to determining the stability of the BH_3OH^- ion solutions as prepared in this laboratory and was carried out at 20° and pH $\geq$ 12.5. In our systems, the hydroxide concentration was always in such a large excess that any changes in hydroxide concentration during the runs were negligible. Thus, the rate data could be interpreted in terms of pseudo-first-order reactions. As did Wang and Jolly,[2] we found the rate of hydrolysis of the BH_3OH^- ion to be pH independent between pH 12.5 and 13.5. However, we found the observed rate constant in this pH range to be 4.93×10^{-5} sec^{-1} as opposed to 1.8×10^{-4} sec^{-1}; that observed by Wang and Jolly.[2] This difference in rate constant is in the expected direction considering the differences in solvents, 88% methanol - water in their study and 100% aqueous in this study. Davis and Gottbrath[5] found the methanolysis of BH_4^- to be 10 times faster than the hydrolysis. The rate constant for the hydrolysis of the BH_3OH^- ion was also measured at different temperatures to obtain the activation energy of the reaction. The rate constants at various pH and temperature are listed in Table II. From a plot of log k_{obs} vs 1/T for the rate constants at 20°, 35° and 50° (pH 13.5), the activation energy was calculated to be 17.4 ± 4.7 kcal/mol. Gardiner and Collat[4c] reported the activation energy for the reaction between BH_3OH^- and H_3O^+ to be 12 ± 9 kcal/mol.

The reaction of nitrous acid with hydrogen peroxide in acidic solution yields peroxynitrous acid.

$$HNO_2 + H_2O_2 \longrightarrow HOONO + H_2O$$

This acid decomposes to nitric acid with a half-time of 7 sec at 0°, but the conjugate base, peroxynitrite ion, is relatively stable in alkaline solutions.[6] The literature procedure for the synthesis of peroxynitrite involves the mixing of an acidic peroxide solution with a nitrite solution, immediately followed by treatment with excess base. Yields of 45-50% have been reported.[7] We have carried out this synthesis with our quenched flow reactor, using equal flow rates of the following solutions at 0°: 0.6 M KNO_2, a solution 0.6 M in HCl and 0.7 M in H_2O_2, and 3 M NaOH. The product solution was analyzed spectrophotometrically.[8] The reaction times (msec) and corresponding percentage yields follow: 44, 44%; 88, 67%; 88, 68%; 230, 77%; 280, 72%; 450, 82%. The relatively low yield obtained for the shortest reaction time (44 msec) was probably a consequence of incomplete reaction of the nitrous acid with the hydrogen peroxide.

Table I. Data for BH_3OH^- Syntheses.

Reaction time, msec	Reagent concn, M BH_4^-	H^+	OH^-	Product temp,[a] °C	Yield of BH_3OH^-,[b] %
26	0.3	0.45	0.6	6	75
21	0.3	0.45	0.6	6	87
16	0.3	0.45	0.6	6	94
10	0.3	0.45	0.6	6	86
16	1.0	2.5	3.0	4	72
20	3.0	4.5	6.0	45	51

[a] Temperature of BH_3OH^- solution. Reagent solutions cooled at 0°.

[b] Determined from amount of H_2 evolved upon complete hydrolysis and boron analysis.

Table II. k_{obs} for hydrolysis of BH_3OH^-.

Temp, °C	OH^-	pH	$T_{1/2}$, min	10^{+5} kobs, sec^{-1}
20	0.032	12.5	233	4.93
20	0.10	13.0	231	4.98
20	0.35	13.5	233	4.96
35	0.35	13.5	68	16.83
50	0.35	13.5	21	80.00

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3. This is admittedly an optimistically low estimate of the activation energy. At -78° the acid-independent hydrolysis of H_2OBH_3 has a rate comparable to that of the acid-dependent hydrolysis.[2] The former reaction would be expected to have an activation energy near 20 kcal/mol, thus making the hydrolysis too rapid for a quenched flow reactor operated near room temperature. We have no explanation for the discrepancy.
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PART I-B: THE REDUCTION OF ORGANIC COMPOUNDS WITH THE HYDROXYBOROHYDRIDE ION

Abstract

Compounds containing functional groups not reduced by or sluggishly reduced by the borohydride ion were treated with the hydroxyborohydride ion, BH_3OH^-, to evaluate the latter as a reducing agent and to allow comparison of its reducing power with that of the borohydride ion. In aqueous solution at pH 11.9 and 0°, ethyl benzoate was reduced to benzylamine at pH 11.7 and 6° in 78% yield. The following ketones were reduced by BH_3OH^- at 0° to alcohols in greater than 70% yield: benzophenone, cyclopentanone, cyclohexanone, 2-methylcyclohexanone, d-camphor, and 4-tert- butylcyclohexanone. Octyl chloride and benzhydril chloride were not reduced by BH_3OH^-.

Introduction

Gardiner and Collat[1] and Wang and Jolly[2] have shown that the hydroxyboroydride ion, BH_3OH^-, is formed during the hydrolysis of the borohydride ion, BH_4^-. In the reduction of esters by aqueous borohydride solutions, Kirsch and Lee[3] observed an increase in the rate of reduction when the borohydride solutions were allowed to age before adding the esters. Using hydrolysis rate constants reported by Gardiner and Collat,[1c] they were able to show that the increased reducing power of the aged borohydride solutions could be explained by the formation of the BH_3OH^- ion, assuming that BH_3OH^- has an effective reducing power greater than that of BH_4. This assumption is consistent with the fact that BH_3OH^- is less stable toward hydrolysis than BH_4^-.

Employing a quenching flow reactor described in a previous publication we have prepared large quantities of alkaline solutions containing the BH_3OH^- ion in concentrations as high as 0.35 M.

The half-life of BH_3OH^- solutions prepared with our reactor is 3.9 hours at 20° and pH $\geq$ 12.5. These alkaline BH_3OH^- solutions contain only small concentrations of unreacted BH_4^- and none of the other intermediate species formed during the hydrolysis of BH_4^-. To determine the utility of the BH_3OH^- ion as a reducing agent, we have in this study examined the reduction of esters, nitriles, nitro compounds, ketones, and alkyl halides.

Results and Discussion

Esters. Esters in which the carbonyl groups are not activated by electron-withdrawing groups are not readily reduced by $NaBH_4$ in organic solvents at ordinary temperatures. However, Brown and Rapoport[5] found that various heterocyclic, aromatic and aliphatic esters are reduced by large excesses of $NaBH_4$ in refluxing methanol. We wished to determine whether a typical unactivated ester, ethyl benzoate, can be reduced by aqueous BH_3OH^- at low temperatures.

The pH of the BH_3OH^- solutions prepared with our quenching flow reactor is 12.5 or above. Initial attempts to reduce methyl and ethyl benzoate with these strongly alkaline solutions at 0° and 25° yielded no reduction products, although the esters were completely consumed, presumably by saponification. We therefore lowered the pH of the BH_3OH^- solutions, hoping to minimize saponification while possibly favoring the conditions for reduction. The pH was adjusted by adding to a vigorously stirred BH_3OH^- solution at 0° sufficient diethylamine-diethylammonium chloride solution (pH 8.5-9.0) to obtain a pH in the range 11-12. The resulting solutions were not well buffered; however the pH changed less than 0.05 unit during the course of the reactions.

We concentrated our efforts on optimizing the reduction of ethyl benzoate. Because ethyl benzoate is essentially insoluble in water, in some experiments we combined it with water-miscible organic solvents to increase the solubility of the ethyl benzoate in the reaction solutions. Experiments were carried out to determine the effectiveness of several water-miscible solvents, hereafter referred to as cosolvents. All the experiments were carried out for 17 hours at 0^o. The molar ratio of BH_3OH^- to ethyl benzoate was 10:1, and the concentration of BH_3OH^- ranged from 0.214 to 0.225 M. When other conditions were held constant, the yield of benzyl alcohol was found to vary somewhat with pH; the yield reached a maximum somewhere in the range pH 11-13. These optimum pH values were determined for several sets of conditions, and the results are summarized in Table I. It can be seen that a good yield (89%) was obtained either using 6% acetonitrile as a cosolvent at pH 11.9 or using no cosolvent at pH 12.6, with an emulsifying agent present. Reaction times longer than 17 hours were explored, but did not result in higher yields of benzyl alcohol. However, more ethyl benzoate was consumed during these longer reaction times because of saponification.

To determine whether hydroxyborohydride gives significantly better yields of benzyl alcohol than borohydride under similar conditions, we carried out a series of experiments to otpimize the yield of benzyl alcohol using aqueous borohydride solutions with a BH_4^- to ethyl benzoate ratio of 10:1. The best yield (11%) was obtained at 0^o and pH 9.8 with a reaction time of 72 hrs. Clearly this yield is much lower than those shown in Table I.

Nitriles. Nitrile groups which have not been activated by electron-withdrawing groups are generally inert to $NaBH_4$. However reduction of nitriles has been achieved at 25^o by using diglyme solutions of $NaBH_4$ and Lewis acids such as $AlCl_3$.[6] We found that benzonitrile is readily reduced to benzylamine by BH_3OH^- solutions at pH 12.5. With a reaction time of either 16 hrs. at 25^o or 48 hrs. at 0^o, the yield was 89% (based on the benzonitrile consumed), and 51-60 percent of the benzonitrile was consumed. The yield was reduced to 83% by going to pH 11.5.

Nitro compounds. Nitro compounds are not reduced to amines by $NaBH_4$. Weill and Panson[7] reported that nitrobenzene is reduced to azoxybenzene by $NaBH_4$ in diglyme at 90^o-100^o, giving only a 55% yield in six hours. We have found that nitrobenzene is reduced to aniline by BH_3OH^-. Four experiments carried out at pH 11.7 and 6^o for five hours, with a BH_3OH^-: nitrobenzene ratio of 10:1, resulted in an average yield of aniline, based on the nitrobenzene consumed, of 78%. The reaction was rather slow; after five hours all the BH_3OH^-, but only 40-47% of the nitrobenzene, had been consumed.

Ketones. Ketones are readily reduced by borohydride at 25^o in hydroxylic solvents.[8] Although hydroxyborohydride would probably seldom be preferred over borohydride for such reductions, we studied the reduction of some ketones with BH_3OH^- solutions at 0^o mainly to verify that BH_3OH^- solutions give good yields of the same reduction products that are obtained with borohydride. Using a molar ratio of BH_3OH^- to ketone of 2:1, an 84% yield of diphenylmethanol was obtained from benzophenone in 15 minutes and an 86% yield of cyclopentanol was obtained from cyclopentanone in 15 minutes. Similar reductions of cyclohexanone, 2-methylcycolohexanone, 4-tert-butylcyclohexanone, and camphor gave 73-74% yields of the corresponding alcohols.

Alkyl Halides. Alkyl halides are inert to $NaBH_4$ in non-aqueous solvents. In aqueous solvents, $NaBH_4$ converts secondary and tertiary alkyl halides to the corresponding hydrocarbons. We attempted the reduction of 1-chlorooctane, 1-iodooctane, and benzyhydryl chloride with BH_3OH^-, but were unsuccessful. No hydrocarbons were isolated.

Experimental

Materials and Techniques. The $NaBH_4$ (Alfa), HCl (J. T. Baker), and NaOH (Mallinckrodt) used to prepare the BH_3OH^- solutions were reagent grade and used as purchased. Most of the organic reagents and solvents were used as received from commercial suppliers; tetrahydrofuran, diglyme, octyl chloride, octyl iodide, ethyl benzoate, benzontrile, nitrobenzene and d-camphor were purified by distillation before use.

During the reduction attempts, no precautions were taken to exclude air, however the reaction mixtures were covered to prevent evaporation. Unless otherwise stated, special beakers, approximately 5 inches tall and 2 1/2 inches in diameter were used as the reaction vessels; thus vigorous stirring was possible without loss of solution from splashing. All glc analyses were carried out on a Varian 1200 gas chromotograph equipped with a flame ionizing detector. The yields were determined from the glc areas by means of calibration curves constructed with internal standards. The method has an accuracy of ±5%.

Preparation of BH_3OH^- Solutions. The BH_3OH^- solutions were prepared with the quenching flow reactor described in Part I-A. The technique involves the mixing of two streams of reactant solutions (BH_4^- and H^+) in a reaction tube with downstream injection of the solution containing an excess of the quenching reagent,

OH^-. The yield of BH_3OH^- is dependent upon the reaction time, i.e., the time between the intial mixing of H^+ and BH_4^- and the quenching with the OH^-. To permit accurate calculation of this time, we introduced calibrated flow meters between the reagent vessels and the reactor. The reagent solutions were precooled to 0° to -5° and were contained in glass-lined stainless steel vessels capable of withstanding pressures of at least 100 psi. The solutions were forced into the reactor by applying pressure from a nitrogen gas cylinder; the flow rates of the three solutions were approximately equal.

By suitable adjustment of the reagent concentrations, and using a reaction time of approximately 16 ms (calculated from the flow rates), we were able to prepare BH_3OH^- solutions containing only small percentages of unreacted BH_4^-. Evidence for the BH_3OH^- ion was obtained from the boron-11 nmr spectrum, which consisted of a 1:3:3:1 quartet, upfield from a borate singlet, with a B-H coupling constant of 92 Hz. The spectrum is in excellent agreement with those recorded by previous workers.[1b,2] The ratio of BH_4^- to BH_3OH^- and other data for representative syntheses are given in Table II. The BH_3OH^- concentration of a solution was determined by measurement of the hydrogen evolved upon heating at 60° for 30 minutes or longer. The BH_4^- content of the solution was then determined from the hydrogen evolved upon addition of excess HCl. The percent yield of BH_3OH^- was calculated from the BH_3OH^- analysis and the boron analysis of a completely hydrolyzed sample.

A 0.35 M solution of BH_3OH^- was used for the boron-11 nmr study. The spectrum was recorded at 0° on a Varian HA-100 spectrometer using a carbon-13 probe and by lowering the magnetic field to resonate for boron-11 at 25.15 MHz.

Esters. The following procedure is representative. An ice-cold solution (35 ml) containing 10 mmol of BH_3OH^- was adjusted to pH 11.9 by the addition of approximately 10 ml of a diethylamine-diethylammonium chloride solution. A solution of 1 mmol of ethyl benzoate in 3 ml of cold acetonitrile was added, and the reaction mixture was stirred at 0° for 17 hours before quenching the reaction by adding excess 1 M HCl. After quenching the reaction, 1 mmol of octyl alcohol (internal standard) was added; the mixture was extracted with three 15-ml portions of diethyl ether, and the combined extracts were analyzed by glc. A 10 ft. long, 1/8 in. o.d. column, packed with 5% Carbowax 20M on acid-washed Chromosorb W support was used.

Benzonitrile. The pH of an ice-cold solution containing 20 mmol of BH_3OH^- was adjusted to 12.5 with ice-cold diethylamine-diethylammonium chloride solution, and a solution of 1.96 mmol of benzonitrile in 5 ml of methanol was added. The reaction mixture was held at 25° and stirred for 16 hours. The mixture was then quenched with 1 M HCl; 1 mmol of valeronitrile was added as an internal standard, and the solution was again made alkaline with NaOH before extracting with three 15-ml portions of diethyl ether. The ether extracts were washed with a known amount of acid to remove the benzylamine as benzylammonium chloride, and the yield of benzylamine was determined by titration of the acidic solution with standard NaOH solution. To check the titration results, the solution was made approximately 1 M in OH^-, a small excess of benzoyl chloride was added, and the precipitated benzyl benzamide was filtered, dried and weighed. Yields of benzylamine determined by these methods agreed within 2%. Unconsumed benzonitrile was determined by glc of the ether extracts using a column of 5% FFAP on Chromosorb G.

Nitrobenzene. Two mmol of nitrobenzene in 5 ml of methanol was added to an ice-cold solution containing 20 mmol of BH_3OH^-. The pH of the solution was adjusted to 11.7, and the reaction mixture was stirred for 5 hours at 6^0. Then the pH was adjusted to approximately 7 by adding a solution of oxalic acid. One mmol of valeronitrile (internal standard) was added; the mixture was extracted with three 15-ml portions of diethyl ether, and the extracts were analyzed by glc utilizing the same column used to analyze for benzylamine.

Ketones. The following procedure for the reduction of benzophenone is representative. An ice-cold solution (25 ml) containing 10 mmol of BH_3OH^- was added to an ice-cold solution of 5 mmol of benzophenone in 35 ml of methanol, and the mixture was stirred. After 15 minutes a white precipitate of diphenylmethanol had formed and the reaction was stopped by adding 1 M HCl. The product was filtered, dried, and weighed: yield, 0.924 g, 84% of theory. After recrystallization from ligroin, the melting point was $67\text{-}69^0$ (lit.[9] 69^0). Diglyme and tetrahydrofuran were used as cosolvents for some of the ketones, with no significant changes in the yields. In the case of cyclopentanone and 2-methyl cyclohexanone, the products were liquids and yields were determined by glc using a column packed with 5% SE-30 on acid-washed Chromasorb W support.

Alkyl Halides. The following procedure is representative of the attempts to reduce alkyl halides. A solution of the halide and decane (internal standard) in ice-cold methanol was mixed with ice-cold BH_3OH^- solution. After 5 hrs. or 48 hrs. (depending on whether the pH was ca. 12.6 or ca. 11.6, resp.) an aliquot of the reaction mixture was quenched with 1 M HCl and extracted with three 15-ml portions of diethyl ether. No octane was found in the extracts, using a glc apparatus and procedure similar to that used in the ketone studies.

Acknowledgements

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Table I. The reduction of ethyl benzoate at optimum pH values

pH	Cosolvent (% v/v)	% yield benzyl alcohol[a]	% consumption ethyl benzoate
11.9	6% CH_3CN	89	97
11.7	4.2% CH_3CN	80	97
11.7	6% t-BuOH	69	99
11.6	4.2% CH_3OH	62	73
11.6	4.2% THF	51	86
12.3	None	89	100
12.6	None; SLS added[b]	89	100

[a] Averaged of several experiments, ±5%.

[b] Solution 3.4 x 10^{-4} M in sodium lauryl sulfate.

Table II. Data for BH_3OH^- Syntheses

BH_4 $\underline{M}$	H^+, $\underline{M}$	OH^-, $\underline{M}$	Product Temp, °C	BH_3OH^-, $\underline{M}$	BH_3OH^-, % Yield	BH_4^-/BH_3OH^-
0.3	0.45	0.6	6	0.091	94	<0.005
1.0	2.5	3.0	4	0.218	72	0.036
1.5	3.0	3.0	6	0.396	86	0.056
1.5	3.0	4.0	6	0.367	68	0.072
3.0	4.5	6.0	45	0.398	51	0.025

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PART II: A KINETIC STUDY OF THE HYDROLYSIS OF THE OCTAHYDROTRIBORATE ION

Abstract

The hydrolysis of the octahydrotriborate ("triborohydride") ion has been studied in cold methanol-water-hydrochloric acid solutions in which the methanol concentration ranged from 0 to 88 percent by volume and the hydrogen ion concentration ranged from 0.25 to 8 M. At -78°, in 88% methanol solutions (0.25 to 8 M H^+), one mole of hydrogen is evolved per mole of $B_3H_8^-$, indicating the formation of $B_3H_7OH_2$. However in 8 M HCl solutions with 0 to 70% methanol, 4.5 moles of hydrogen per $B_3H_8^-$ were obtained at -78°. Upon warming any of the solutions to room temperature, complete hydrolysis took place, giving additional hydrogen to make a total of 9 moles of hydrogen per mole of $B_3H_8^-$.

The $B_3H_7OH_2$ was converted to $B_3H_7OH^-$ by the addition of hydroxide. However, $B_3H_7OH^-$ was found to be unstable, decomposing to give BH_4^- and $B(OH)_4^-$ at temperatures above -41°. In strong base (2 to 16 M OH^-), and an elevated temperatures, $B_3H_8^-$ solutions also decompose to hydrogen, BH_4^- and $B(OH)_4^-$. The boron-11 nmr spectrum of $B_3H_7OH^-$ consists of two bands with an intensity ratio of 1:2, centered 10.22 ppm downfield and 39.29 ppm upfield from the borate signal, respectively.

Introduction

The hydrolysis of the octahydrotriborate ion, $B_3H_8^-$, in cold-methanol-water solution was studied by Wang and Jolly.[1] They reported that at -78°, the hydrolysis in 1.0-3.5 M HCl yielded one mole of hydrogen per mole of $B_3H_8^-$, corresponding to the formation of B_3H7OH_2. However, in aqueous 8 M MCl, hydrolysis produced 4.5 moles of hydrogen per mole of $B_3H_8^-$ at -78°. The purpose of this work was to study the hydrolysis over an expanded range of hydrogen ion concentration and try to determine the sequential mechanism of the hydrolysis in cold acid solutions.

Experimental

General. Sodium borohydride (Ventron) and iodine (Mallinckrodt) were used as received without further purification. Absolute methanol, hydrochloric acid, potassium hydroxide and sodium hydroxide were all reagent grade. Tetrahydrofuran and p-dioxane were dried by refluxing with and distilling from sodium benzophenonate, and diglyme was dried by distilling from $LiAlH_4$.[2] Raman spectra were recorded on a JOBIN YVON Ramanor HG,2S Raman Spectrophotometer, and infrared spectra were obtained with a Perkin-Elmer spectrometer (Model 337). The boron-11 spectra were recorded at 57.78 Mg Hz on a spectrometer which included the Bruker 42 kilogauss superconducting magnet, and Nicolet 1180 data system.

Synthesis of KB_3H_8. Sodium octhydroborate was prepared by the reaction of iodine with sodium borohydride.[3] The dioxanate of NaB_3H_8 was precipitated from diglyme along with NaI and any unreacted $NaBH_4$. The mixture of salts was dissolved in a minimum amount of water, and the potassium octahydroborate was precipitated and isolated as described by Wang.[1] After purification, hydrogen analysis showed the salt to be 99.7% pure and potassium analysis (precipitation of potassium tetraphenylborate) indicated 99.4% purity. Boron analysis by the mannitol method (a relatively inaccurate method) gave a purity of only 98%.

Kinetic Studies

Acidic Solutiions. A fragile bulb containing 0.5-2 mmol of KB_3H_8 dissolved in 2 ml of 88% methanol-water, was lowered into the reaction vessel[3] which was pre-cooled to -78°. The reaction vessel contained a known amount of HCl dissolved in the same solvent, always maintaining a volume of 30 ml, so that the final volume of the reaction mixture would not exceed 32 ml upon addition of the 2 ml of KB_3H_8 solution. After about 25 minutes it was assumed that the solution in the fragile bulb had cooled to -78^0 and the system was evcacuated. Then the system including a manometer, was closed to the vacuum pump; the fragile bulb was broken, and a timer was turned on. The rate of reaction was obtained as a function of time by momentarily closing a stopcock between the manometer and the reaction vessel, and recording the mercury level of the manometer. When the rate of reaction was relatively great, the reaction was followed to completion and the total hydrogen was measured by Toeplering it into a calibrated volume. In some of the runs, with $[H^+]$ = .25, 1.0, 1.25, 3.0, 4.0, and 8.0 M, after hydrogen evolution had ceased at -78^0, the -78^0 bath was replaced with a chlorobenzene slush, -45^0, and the rate of hydrogen evolution was followed as a function of time as described above.

Basic Solutions. In the kinetic run carried out to determine the rate of reaction of KB_3H_8 with strong base as a function of KB_3H_8 concentration, a known amount of the salt was added to a Kel-F-lined reaction vessel containing 5 ml of either 10 or 15 M NaOH. The vessel was connected to a gas buret and placed in a 50^0 thermostated bath. After the temperature of the system had equilibrated, the system was closed and a timer was turned on. The reaction mixture was stirred vigorously with a magnetic strirrer and a Teflon-covered magnetic stir bar. The change in the water level of the gas buret was recorded at measured intervals until at least 3/4 of the expected hydrogen had been evolved. In initial-rate studies, designed to determine the dependence of the rate of reaction on OH^- , 3 ml of NaOH of the desired concentration was placed in Section A of the reaction vessel shown in Figure 1, 1 mmol of KB_3H_8 was added along with a special Teflon coated magnetic bar, and Section A was connected to Section B with an o-ring joint and the assemblage was placed in a 60° thermostated bath as illustrated in Figure 1. The initial rate of reaction was determined by measuring the rate of movement of the drop of water.

Synthesis of $B_3H_7OH^-$. A fragile bulb containing 1 mmol of KB_3H_8 in 2 ml of 88% methanol-water was lowered into a reaction vessel[3] containing 3 ml of the same solvent which was 2 M in HCl. The reaction vessel was cooled to -78° and then evacuated. The fragile bulb was broken, and the reaction was allowed to processed for 30 hours. At this time, 35 ml of 0.5 M NaOH (in 88% methanol-water), pre-cooled to -78°, was added. In the reactions designed to determine if any hydrogen was evolved upon addition of NaOH, the reaction was carried out in a reaction vessel designed to accomodate 2 fragile bulbs.[3] After 30 hours, the hydrogen produced was removed and the fragile bulb containing 15 ml of 0.5 M NaOH was broken. The reaction vessel was opened to the Toepler pump and checked for hydrogen.

The $B_3H_7OH^-$ was characterized by boron-11 nmr and by the amount of hydrogen evolved upon the addition of excess acid. Because the boron-11 nmr analysis required locking on a deuterium signal, the above mentioned experiments were also carried out in 88%-12% methanol D_2O mixtures.

Determination of Boric Acid. The reaction vessels used are shown in Figure 2. Six ml of 10 M HCl (20% methanol by volume) was added to Section A of reaction vessle I along with a Teflon-coated magnetic stir bar. One ml of 88% methanol-water containing a known amount of KB_3H_8 was then added to Section B of reaction vessel I and the vessel was placed in a Styrofoam box. The Styrofoam box was filled with pulverized dry ice and a lid was taped on top of the box to prevent rapid evaporation of the dry ice and to prevent spillage of the dry ice upon tilting. A hole in the lid allowed the 24-40 joint of vessel I to protrude and be connected to an oil bubbler. After 30-45 minutes, the cold solutions were mixed by tilting the box, forcing the contents of Section B into Section A. The box was swirled while tilting allowing the motion of the stir bar to aid the mixing of the 2 solutions. After approximately 12 hours, the lid was removed from the Styrofoam box and vessel I was connected to vessel II by way of 24/40 joints. Another Styrofoam box was taped to the first box containing vessel I and additioinal pulverized dry ice was added. The Styrofoam box was inverted (see insert of Figure 2) and the solution filtered by suction through the frit into reaction vessel II. The boxes were then separated, the dry ice carefully removed and the reaction vessels were separated. The solid and solution adhering to the sides of vessel I were carefully washed into a 100-ml round-bottomed flask, and the washings were titrated for hydrogen ion concentration using para-nitrophenol as the indicator. Excess base was then added to make sure that all the boric acid present was converted to borate. The solution was then analyzed for boron according to the procedures for analysis of boron in the presence of methanol.[4] The solution in reaction vessel II was washed into a 100-ml round-bottomed flask and also was analyzed for HCl and boron.

In order to determine the solubility of boric acid in the methanolic solvents used, saturated solutions of boric acid were prepared using solvents with methanol-water ratios identical to those in the afore-mentioned experiments. These saturated solutions were cooled to and filtered at -78° (the solubility was considerably less at -78°) and after the clear solutions had been warmed to room temperature, aliquots were taken and analyzed for boron according to the procedures of reference 4.

Low Temperature Raman and NMR Studies. The reaction of KB_3H_8 with 10 M HCl solutions was allowed to proceed for approximately 12 hours at -78° before collecting the samples for the spectra. Collection of the Raman sample was accomplished by connecting a special low temperature cell, via the 14/35 ground joint, to vessel II of Figure 2 while the dry ice box was still intact. Dry ice was packed around the cell, secured with aluminum foil, and the solution poured into the cell by appropriately tilting the dry ice box. For the low temperature nmr studies, the cold, -78°, solutions were pipetted with a dry ice-jacketed pipet and transferred to a previously cooled, 10-mm quartz nmr tube. The nmr tubes and the special Raman cells were stored in dry ice-acetone baths until they were ready to be placed into the respective spectrometers.

Results and Discussion

Acidic Solutions. In cold (-78°) 88% methanol solutions, with the hydrogen ion concentration in the range 0.20-8 M, the hydrolysis of KB_3H_8 yields one mole of hydrogen per mole of $B_3H_8^-$. Ratios of hydrogen produced per mole of $B_3H_8^-$ consumed are listed in Table I. The total amount of hydrogen evolved was determined experimentally, when the rate of reaction permitted it, by following the rate of hydrogen evolution as a function of time until the hydrogen evolution ceased. The hydrogen was then Toeplered into a known volume and measured, with the yield being based on the amount of KB_3H_8 consumed. The KB_3H_8 salt used in this study was always at least 99.7 percent pure. In the runs where H^+ = 1.0, 1.50 and 2.95 M, the total amount of hydrogen produced per $B_3H_8^-$ consumed was verified to be 1.0 by using Eq. (1),

$$\frac{H_2}{B_3H_8^-} = \frac{9P_1}{P_1 + P_2} \qquad (1)$$

where P_2 is the computer-calculated P obtained upon fitting the rate data from the hydrolysis of $B_3H_7OH_2$ at -45° to a least squares program, assuming first-order reactions and P_1 is the calculated P obtained in the same manner from the rate data for the hydrolysis of $B_3H_8^-$ at -78°. Since complete hydrolysis of $B_3H_7OH_2$ yields eight moles of hydrogen, (see reaction (6)), $(P_1 + P_2)$, the total amount of hydrogen evolved in the reactions at -45° and -78°, should be nine times the total amount, P_1, produced in the reaction at -45°. This being the case, the right hand side of Equation (1) should always be 1. The ratio of H_2 to $B_3H_8^-$ was calculated to be 1.04, 1.05 and 1.04 for the runs where H^+ = 1.0, 1.5 and 2.95 M respectively. One mole of hydrogen per mole of $B_3H_8^-$ consumed corresponds to the formation of $B_3H_7OH_2$, according to reaction (2).

$$B_3H_8^- + H^+ + H_2O \xrightarrow[-78°]{k_1} B_3H_7OH_2 + H_2 \qquad (2)$$

The $B_3H_7OH_2$ formed is very stable at -78° in 88% methanol-water solutions at $[H^+] \leq 8$ M. However, in 8 M HCl solutions containing methanol concentrations in the range of 0-70 percent by volume, the reaction proceeds further at -78° to give a total of 4.5 moles of hydrogen per mole of $B_3H_8^-$ consumed. The data in Table II show that one-half the total amount of hydrogen evolved upon warming the solutions to room temperature is evolved at -78°. The rate of reaction at -78° varied with changes in the methanol concentration (% v/v). The reaction half-time (time required for one-half the total mount hydrogen produced at -78°), as a function of percent methanol used is also listed in Table II.

We studied the rate of reaction (2) as a function of hydrogen ion concentration in solutions with and without the addition of LiCl. Appropriate amounts of LiCl were added to solutions that were 0.20-1.5 M HCl in order to maintain a constant ionic strength of 1.5. The runs where no LiCl was added in order to maintain constant ionic strength were carried out in solutions where the hydrogen ion concentration ranged from 0.25-1.25 M. In all the runs, with the exception of those in 0.20 and 0.25 M HCl, the hydrogen ion concentration was at least ten times the $B_3H_8^-$ ion concentration allowing the rate data to be interpreted in terms of pseudo-first-order reactions. A typical set of pressure data is listed in Table III, and a semi-logarithmic plot of $(P_\infty - P)$ versus time for the data is shown in Figure 3. The fact that $\log(P_\infty - P)$ versus time is linear indicates that reaction (1) is first order with respect to $B_3H_8^-$ ion concentration. The observed rate constants, k_1, were obtained at $[H^+] = 0.25$, 0.60, 1.0, and 1.25 M and are listed along with the concentration of $B_3H_8^-$ in Table IV. Since the hydrogen ion concentration did not remain constant during the course of the run, the rate constant at $[H^+] = 0.25\ \underline{M}$ were calculated, using Eq. (3) which was arrived at by integration of the rate expression

$$k_1t = \frac{1}{[H^+]_0 - [B_3H_8^-]_0} \ln \frac{[B_3H_8^-]_0([H^+]_0 - x)}{[H^+]_0([B_3H_8^-]_0 - x)} \quad (3)$$

In Eq. (3) $[B_3H_8^-]_0$ and $[H^+]_0$ correspond to the initial concentrations of the reagents, and $([B_3H_8^-]_0 - x)$ and $([H^+]_0 - x)$ correspond to the concentration of the reagents at time t. The quantity x, corresponds to the amount of hydrogen produced at time t, and as is seen from reaction (1) is equal to the amount of $B_3H_8^-$ consumed at time t. In order to determine the amount of $B_3H_8^-$ present at any time t, computer-calculated values of P_∞ were obtained by assuming that the reaction was first-order in $B_3H_8^-$ concentration and by assuming that the hydrogen ion concentration did remain constant during the course of the runs. P_∞ is proportional to the total amount of $B_3H_8^-$ used. Therefore, the value of x, in units of concentration was calculated using Eq. (4).

$$x = \frac{P(\text{mmol } B_3H_8^-)}{P_\infty(\text{vol. of reaction mixture})} \quad (4)$$

The rate constant k_1 obtained from plotting the right hand side of Eq. (3) versus time is a second-order rate constant with a value of $1.68 \times 10^{-3}\ \underline{M}^{-1}\ \text{min}^{-1}$. Multiplying by the hydrogen ion concentration, $0.25\ \underline{M}$, gives the first-order rate constant listed in Table IV, 4.20 x 10^{-4} min^{-1}. A plot of k_1 versus hydrogen ion concentration (see Figure 4) is linear with a zero intercept at $[H^+] = 0$ and indicates the following rate law for reaction (2),

$$-\frac{d[B_3H_8^-]}{dt} = k_{1a}[B_3H_8^-][H^+] \qquad (4)$$

where the value of $k_{1a} = 2.88 \times 10^{-3}$ $\underline{M}^{-1}$ min^{-1}. Thus, the hydrolysis of the triborohydride ion in 88% methanol-water solutions where $[H^+] \leq 1.25$ $\underline{M}$ at -78° is first-order in triborohydride ion and hydrogen ion concentration. An attempt to determine the value of k_{1a} of Eq. (4) at constant ionic strength resulted in observed rate constants, k_1' that when plotted versus hydrogen ion concentration gives a straight line but the intercept at $[H^+] = 0$, is a somewhat large negative number. This relatively large negative intercept at $[H^+] = 0$ indicates that the hydrogen ion concentration of the solutions are actually lower than the calculated values. A close examination of the preparation of solutions identical to those used for the kinetic study revealed that a gas was evolved upon the additional of methanol to a mixture of aqueous hydrochloric acid and LiCl. Also attempts to prepare hydrochloric acid solutions with hydrogen ion concentrations in excess of 8.3 $\underline{M}$ in 88% methanol-water failed, presumably because of the formation of methyl chloride.[6] Since the formation of alkyl halides are catalyzed by Lewis acids, it is likely that the LiCl acted as a catalysis, aiding the production of CH_3Cl. Since CH_3Cl boils at 24°, it is possible that it would have vaporized out of solution when the solutions were prepared at room temperature, or it could have been pumped out of solution when the systems were evacuated, while being stirred at -78°.

Therefore, we were unable to determine the dependence of reaction (2) on hydrogen ion concentration at constant ionic strength. The values of k_1' are also listed in Table IV as a function of hydrogen ion concentration.

Extrapolation of the data in Table IV to $[H^+] = 3.0$ M, should give a rate constant with a half-life of not less than one-half hour. However, we found the rate of hydrogen evolution in 3 M HCl to be too fast to measure accurately; the half-life of the reaction was approximately two minutes. The rate increased even more upon increasing the hydrogen ion concentration to 4 and 8 M HCl; the half-life of the reaction in 4 M HCl was less than one minute. This tremendous increase in the reaction rate implies that the rate of hydrolysis for reaction (2) in solutions were $[H^+] > 3$ M is far more complex than first-order. However, the reaction, even though more complicated, did not proceed beyond the formation of $B_3H_7OH_2$ (see Table I for the ratio of hydrogen produced as a function of $B_3H_8^-$ consumed).

The fact that we were able to measure the rate of hydrolysis of $B_3H_8^-$ to $B_3H_7OH_2$ indicates that $B_3H_8^-$ is more stable toward hydrolysis than BH_4^-. Wang and Jolly[5] found that the first step of the hydrolysis of BH_4^- to BH_3OH_2 is too fast to measure in cold (-78°) 88% methanol-water hydrochloric acid solutions at hydrogen ion concentrations as low as 0.11 M.

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

$$B_3H_7OH_2 + 8\ H_2O \xrightarrow[-45^\circ]{k_2} 3B(OH)_3 + 8\ H_2 \qquad (5)$$

We studied the rate of reaction (5) as a function of hydrogen ion concentration. In all the runs the hydrogen ion concentration was in excess, permitting the interpretation of the data as pseudo-first-order reactions. We obtained observed rate constants for reaction (5) for hydrogen ion concentrations from 0.25 to 8 <u>M</u>. Semi-logarithmic plots of $(P_\infty - P)$ vs time for the data obtained in solutions were $[H^+] \leq 3$ <u>M</u> are linear. Such a plot for the run at -45° and $[H^+] = 1.5$ <u>M</u> is shown in Figure 5. The fact that log $(P_\infty - P)$ versus time is linear, implies that reaction (5) is first-order with respect to the concentration of $B_3H_7OH_2$. Computer-calculated values of k_2 were obtained by using a least squares program capable of solving the first-order reaction function, $X = [A]_0(1 - e^{-k_2t})$, where $[A]_0$ is the initial concentration of $B_3H_8^-$ which is proportional to the total amount of hydrogen evolved, P_∞, and X is the amount of $B_3H_8^-$ consumed at time t, or P, the pressure of hydrogen at time t. The observed rate constants, k_2, are listed as a function of hydrogen ion concentration in Table V. The values of k_2 indicate that reaction (5) is independent of hydrogen ion concentration in acidic solutions where $[H^+] \leq 1.5$ <u>M</u>, and is effected by hydrogen ion concentration in solutions where $[H^+] \geq 1.5$ <u>M</u>. Semi-logarithmic plots of $(P_\infty - P)$ vs time for the data obtained in 3.5, 4, and 8 <u>M</u> HCl at -45° are not linear. We attempted to interpret the rate data in these runs in terms of pseudo-second-order reactions and found that $1/(P_\infty - P)$ is a linear function of time for the 4 and 8 <u>M</u> HCl rate data but was non-linear for the 3.5 <u>M</u> HCl data. A plot of $1/(P_\infty - P)$ for the 4 <u>M</u> HCl rate data is shown in Figure 6. The change in reaction order upon going from 3 to 4 <u>M</u> HCl, plus the fact that the observed rate constants, k_2 is, within experimental error, independent of hydrogen ion concentration in dilute acid solutions, $[H^+] \geq 1.5$ M, suggest that the rate law for reaction (5) can be expressed by Eq. (6).

$$\frac{-d[B_3H_7OH_2]}{dt} = k_{2a}[B_3H_7OH_2] + 2k_{2b}[B_3H_7OH_2]^2\ [H^+] \qquad (6)$$

Since the hydrogen ion concentration remained constant during the course of the runs, this rate law implies that the hydrolysis of $B_3H_7OH_2$ proceeds according to the following general reactions,

$$A \xrightarrow{k_2} \text{Products}$$

$$A + A \xrightarrow{k_3} \text{Products}$$

where $A = B_3H_7OH_2$, $k_2 = k_{2a}$, and $k_3 = k_{2b}$.

The rate of disappearance of A, $B_3H_7OH_2$, is described by the following equation, where the amount of reactant present at zero time is $[A]_0$ and at time t is $([A]_0 - X)$:

$$-\frac{d([A]_0 - X)}{dt} = k_2([A]_0 - X) + 2\ k_3([A]_0 - X)^2 \qquad (7)$$

rearrangement leads to:

$$\frac{dx}{([A]_0 - X)[k_2 + 2\ k_3([A]_0 - X)]} = dt \qquad (8)$$

The intergrated rate expression[7] can be written as

$$\ln\left[\frac{[A]_0[k_2 + 2\ k_3([A]_0 - X)]}{([A]_0 - X)[k_2 + 2\ k_3[A]_0)]}\right] = k_2t \qquad (9)$$

or

$$X = [A]_o - \left\{ \frac{[A]_o\, k_2}{k_2 + 2\, k_3[A]_o} \left[e^{k_2 t} - \frac{2\, k_3[A]_o}{k_2 + 2\, k_3[A]_o} \right]^{-1} \right\} \qquad (10)$$

During the runs, the extent of the reaction was following by monitoring the increase in hydrogen pressure as a function of time. Therefore, in Eqs. (7)-(10), $[A]_o = P_\infty$, the pressure at time t = infinity, and $X = P$, the pressure at time t. Rewriting Eq. (11) gives:

$$P = P_\infty - \left\{ \frac{P_\infty k_2}{k_2 + 2\, k_3 P_\infty} \left[e^{k_2 t} - \frac{2\, k_3 P_\infty}{k_2 + 2\, k_3 P_\infty} \right]^{-1} \right\} \qquad (11)$$

The parameters P_∞, k_2 and k_3 were evaluated from the data in Table VI using a least-squares program. The computer-calculated values were 32.20 cm Hg, 6.89×10^{-3} min^{-1}, and 6.99×10^{-3} $\underline{M}^{-1}$ min^{-1} for P_∞, k_2, and k_3 respectively. We also evaluated P_∞, k_2 and k_3 from the rate data as a function of hydrogen ion concentration and obtained the values listed in Table VII. The negative values of k_3 in the dilute acid runs, $[H^+] \leq 1.5$ $\underline{M}$ are, within experimental error, equal to zero or a small positive number. We calculated the k_2 values listed in Table VII for the runs where $[H^+] < 2.95$ $\underline{M}$ using Eq. (11) by setting $k_3 = 0$. These values are also listed in Table VII, and as expected are exactly equal to the k_2 values listed in Table V. As can be seen from the k_2 values, the small positive number (1.04×10^{-1} $\underline{M}^{-4}$ min^{-1}) of k_3 for the 2.95 $\underline{M}$ run did not change the value of k_2 for that run, supporting the hypothesis that k_3 in the dilute acid solutions, $[H^+] \leq 1.50$ M, is, within experimental error, equal to zero.

The values of k_2 for the 3.5, 4.02 and 8.03 M HCl runs indicate that in this region, the hydrolysis of $B_3H_7OH_2$ at -45° is approximately first-order in hydrogen ion concentration. The values of k_3 in this hydrogen ion concentration region is difficult to rationalize on the basis of the rate law of Eq. (6). These k_3 values, along with the tremendous increase in the first-order rate constant k_2, on going from 1.5 to 3 M, could be due to the activity of the hydrogen ion. In all our calculations, we are assuming that the activity of the hydrogen ion in 88% methanol-water is the same as the activity in 100% water. We were only able to find acidity functions for dilute acid solutions in various methanol concentrations, however, in methanol-water mixtures above 60% methanol, the effect of the methanol increased the acidity, the proton donating ability, of the hydrochloric acid solutions, indicating that the activity in 88% methanol-water is not at all the same as it is in 100% water. Salomaa[8] reported that as the concentration of acid increased the effect of the methanol became more pronounced. He found that the acidity function H_0, for 0.08 M HCl was 1.86 in 65% methanol and 1.80 in 88% methanol, and that the acidity function for 0.80 M HCl was 0.85 in 65% methanol and 0.75 in 88% methanol, (H_0 decreases with increases acidity). If the acidity of the solutions in our study follow the same trend, this could attribute to the observed increase in the rate of hydrolysis for both reaction (2) and (5) upon increasing the hydrogen ion concentration above 1.5 M.

At -78° in 8 M HCl solutions containing from 0 to 70% methanol by volume, 1 mole of hydrogen per mole of KB_3H_8 is evolved in approximately 2 minutes, corresponding to the formation of $B_3H_7OH_2$. This species further hydrolyzes at -78° to give a total of 4.5 moles of hydrogen and an unknown boron-hydrogen intermediate which, when warmed to room temperature, gives another 4.5 moles of hydrogen corresponding to complete hydrolysis of $B_3H_8^-$.

$$B_3H_8^- + H^+ + 9\ H_2O \longrightarrow 3\ B(OH)_3 + 9\ H_2 \qquad (12)$$

The rate of hydrolysis is essentially equal in 8 M HCl solutions containing various percentages of methanol up to 65% methanol by volume. The reaction half-time, that is, the time required for evolution of one-half of the total amount of hydrogen evolved at -78° as a function of methanol is listed in Table II.

Close examination of the 8 M HCl solutions at -78° revealed that, in addition to the formation of the unknown boron-hydrogen intermediate, an appreciable amount of solid collected in the reaction flask during the course of the reaction. Using the apparatus shown in Figure 2, we filtered the reaction mixture at -78°, collected the solid, and dried it at room temperature over KOH in a vacuum dessicator. Infrared spectra of the solid were identical to spectra taken of reagent grade $B(OH)_3$ with fundamentals at 3200, 1195, and 645 cm^{-1} corresponding to OH vibrations and fundamentals at 1450, 880, and 545 cm^{-1} corresponding to various BO vibrations.[9] Knowing that the hydrolysis produced both boric acid and 4.5 moles of hydrogen, we attempted to determine the stoichiometry of the unknown boron-hydrogen intermediate by determining X in the following equation:

$$B_3H_8^- \xrightarrow[-78^\circ]{8\ HCl} X\ B(OH)_3 + \text{"B-H"} + 4.5\ H_2 \qquad (13)$$

Using Schreinemakers[10] wet residue method of analysis, we determined the amount of $B(OH)_3$ produced in Eq. (13) as a function of the "dryness" of the solid collected at -78°. Here "dryness" is defined as the fraction of the solution sucked through the frit of vessel I into vessel II (Figure 2). Because in all the runs the acid concentration was several hundred times the concentration of KB_3H_8, and therefore remained constant during the course of the runs, the "dryness" was calculated by titrimetric analysis of the hydrogen ion in vessel I, H_a^+, and the hydrogen ion in vessel II, H_b^+, using Eq. (14).

$$\text{"dryness"} = D = \frac{H_b^+}{H_a^+ + H_b^+} \qquad (14)$$

The amount of $B(OH)_3$ produced was determined by titrating the solution from vessel I for boron using the mannitol procedure of reference 4. The amount of $B(OH)_3$ produced was corrected for the solubility of boric acid in the solvent used. The ratio of the amount of boric acid produced to the amount of KB_3H_8 consumed is summarized in Table VIII and is plotted versus "dryness" in Figure 7. Extrapolation of the line of Figure 7 to complete "dryness", $D = 1$, indicates that 0.96 ± 5% mole of $B(OH)_3$ are produced per mole of $B_3H_8^-$.

Setting $X = 1$, the reaction of equation (13) can be balanced and rewritten as shown in equation (15).

$$B_3H_8^- + H^+ + 3H_2O \xrightarrow[-78^\circ]{8\ \underline{M}\ HCl} B(OH)_3 + \text{"}B_2H_3\text{"} + 45\ H_2 \qquad (15)$$

Raman spectra of the solution containing the "B_2H_3" species were recorded at -78° in hopes of obtaining structural information concerning the species. Since the solvent used in the boric acid determinations contained ~ 20% methanol, we compared the spectra of the solvent saturated in boric acid, and the spectrum of the solution shown in Figure 8 to literature spectra of aqueous solutions of boric acid and methyl borate.[11,12] In Figure 8, the signal at 2430 is the only absorption band other than those found in a sample of the solvent saturated with boric acid. This is in the region, 2400-2500, common to B-H stretching frequencies in boron-hydride compounds containing terminal hydrogens such as $(CH_3)_3NBH_2NCCH_3^+$[13] or $(CH_3)_3NBH_2ON(CH_3)_3^+PF_6^-$.[14] However, the very intense absorption usually observed at 1150 cm^{-1} which corresponds to BH_2^+ deformation was not observed in our spectra. The bands in the spectrum of Figure 8 are assigned as summarized in Table IX. Low temperature ^{11}B nmr spectra of the solution containing the "B_2H_3" species contained no apparent peaks. However, there appeared to be a very broad signal present, unresolvable from the base line, which was on the order of several thousand Hz wide.

We followed the rate of hydrolysis of $B_3H_8^-$ in 8 $\underline{M}$ HCl solutions of various methanol concentrations and found that a semi-logarithmitic plot of $(P_\infty - P)$ for data such as that in Table X versus time were curved rather than linear. Assuming that the first step of the hydrolysis corresponds to the formation of $B_3H_7OH_2$, we postulated that further hydrolysis of $B_3H_7OH_2$ proceeded through an unknown intermediate to give 3.5 moles of hydrogen and, according to the results of the boric acid determination, one mole of $B(OH)_3$ per mole of $B_3H_7OH_2$. Assuming that the hydrolysis of $B_3H_7OH_2$ in these solutions proceed by way of two conseutive first-order reactions, we can write the following general equations,

$$A \xrightarrow{k_4} B + nH_2$$

$$B \xrightarrow{k_5} C + mH_2$$

where k_4 and k_5 are pseudo-first-order rate constants and n and m are proportional to the total number of moles of hydrogen, 3.5, produced in each step. Since the rate of hydrolysis was monitored by following the hydrogen pressure as a function of time, the factor C is used to convert pressure of hydrogen into the corresponding solution concentration and the following equations are obtained.

$$(P_\infty - P_0)\,C = n[A]_0 + m[B]_0$$
$$(P - P_0)\,C = n[A]_0 - n[A] + m[B]_0 - m[B]$$

The integrated rate expressions[7] for two consecutive first-order reactions lead to:

$$[A] = [A]_0\, e^{-k_4 t}$$

$$[B] = [B]_0 + \frac{k_4[A]_0}{k_4 - k_5}\, e^{-k_5 t} - \frac{k_4[A]_0\, e^{-k_4 t}}{k_4 - k_5}$$

If at time $t = 0$, $[B]_0/[A]_0 = x$, the four preceeding equations can be combined with the relation $[B]_0 = x[A]_0$ to give,

$$P = P_{\infty} - \left[\frac{(P_{\infty} - P_0)}{n + mx}\left[\left(\frac{n(k_4 - k_5) - mk_4}{k_4 - k_5}\right)e^{-k_4 t} + \left(mx + \frac{mk_4}{k_4 - k_5}\right)e^{-k_2 t}\right]\right] \tag{16}$$

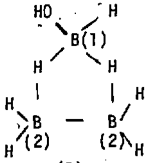
Using the rate data where the difference in k_4 and k_5 is greatest, the 70% CH_3OH rate data of Table X was used to calculate the parameters, n, m, x, k_4 and k_5 by using a least squares program capable of solving non-linear functions. In order to calculate the above mention parameters, some assumptions had to be made and the rate data appropriately adjusted. First, since during the kinetic runs, it was always observed that within two minutes after the fragile bulb containing the $B_3H_8^-$ ion was broken and the triborohydride mixed with the HCl solutions, a sudden surge of hydrogen was produced which corresponded to one mmol of gas per mmol of $B_3H_8^-$ consumed, the pressure at time $t = 0$ P_0, was taken to be $P_{\infty}/4.5$. P_{∞} was obtained experimently by waiting 12 to 18 hours after evolution of the hydrogen became immeasurable. The pressures and time were adjusted by subtracting P_0 and t_0 from the values listed in Table X and these calculated values of P and t were used to solve the function of equation (16). The best fit of the data to the function was achieved when $n = 3.0$, $m = 0.5$, $x = 0.081$, $k_4 = 6.62 \times 10^{-3}$ min^{-1} and $k_5 = 2.86 \times 10^{-3}$ min^{-1}. This ratio of n to m does not shed any light on the composition of the unknown boron-hydride species produced along with one mole of $B(OH)_3$ and 4.5 moles hydrogen per mole of $B_3H_8^-$ consumed.

When these solutions containing the unknown boron-hydride species are warmed to -36°, another 4.5 moles of hydrogen per mole of $B_3H_8^-$ are evolved in approximately 12 hours. The rate data in Table XI were obtained after warming the same solution which gave the 70% CH_3OH data in Table X to -36°. We again assumed that the hydrolysis of the unknown species proceeded by way to two consecutive first-order reactions and used the same function in equation (17) to solve for the rate constants, k_6, and k_7, the ratio of the two unknown species at time $t = 0$, x, and the values of n and m assuming $n + m = 4.5$. The values of the parameters were 0.038, 3.5, 1.0, $2.3 \cdot 10^{-2}$ min^{-1}, and 3.98×10^{-3} for x, n, m, k_6, and k_7, respectively. The calculated value of 1.0 for m agrees with the observations of Wang,[1] namely; he compared the rates of hydrolysis of the unknown boron-hydrogen intermediates at -49.4°, -43.5°, -38.4° and -35.6° with those of a $BH_2(H_2O)_2^+$ solution, by plotting $\log(P_\infty - P)$ versus time for both cases. Since the $BH_2(H_2O)_2^+$ species hydrolyzes through the $H_2OBH(OH)_2$ species, a plot of $\log(P_\infty - P)$ versus time is non-linear where the initial slope of the curved line is proportional to the hydrolysis of $BH_2(H_2O)_2^+$ to $H_2OBH(OH)_2$ and the final slope of the curved line in proportional to the hydrolysis of $H_2OBH(OH)_2$ to boric acid. Wang found that the initial slopes of the two plots indicate that if the unknown mixture contains $BH_2(OH_2)_2^+$, it is not the only species present. However, the final slopes of the plots indicate that the hydrolysis involves $H_2OBH(OH)_2$ immediately before the formation of boric acid. Therefore, from this study by Wang, and the results of this present work, we can say that the final step of the hydrolysis of $B_3H_8^-$ in 8 M HCl solutions containing from 0 to 70% methanol by volume, proceeds through a boron-hydrogen species capable of evolving only one mole of hydrogen and this species is most likely $H_2OBH(OH)_2$.

Because of the complexity of the hydrolysis, which may be due to the activity of the relatively concentrated hydrochloric acid solutions in 88% methanol-water solutions at -78, we are unable to propose a mechanism for the hydrolysis of the triborohydride ion, $B_3H_8^-$, in these cold methanolic acidic solutions.

Alkaline Solutions. Since H_2OBH_3 is deprotonated by the addition of strong base, forming BH_3OH^-, we postulated that $B_3H_7OH_2$ could likewise be deprotonated. We added excess base to a solution containing $B_3H_7OH_2$ at -78°, and observed no decomposition due to hydrolysis (evidenced by no hydrogen evolution). A boron-11 nmr spectrum of such a solution recorded at -78° showed only 2 broad peaks in a ratio of 1:2 centered ~10.1 ppm downfield and ~39.2 ppm upfield, respectively, from the peak due to the trace of borate present. The spectrum remained unchanged up to -65°, and a spectrum recorded at -65° is shown in Figure 9. The split signal at approximately zero Hz (illustrated in the insert of Figure 11), is that of the methoxyborate derivatives expected to exist in alkaline methanol solutions. We observed that in aqueous base, the spectrum of borate consist of one sharp peak (set to zero for reference purposes); however, upon addition of methanol to the aqueous solutions, the signal at approximately zero ppm is split, presumably because of the formation of methoxyborate species corresponding to the general formula $B(OH)_{4-x}(OCH_3)_x^-$.

The two broad peaks at -10.1 and +39.2 ppm can be assigned to the two different types of boron in $B_3H_7OH_2$ if the structure of $B_3H_7OH_2$ is represented as I.



(I)

Two different types of borons were observed by Dolan et al[15] in $B_3H_7NCCH_3$; however the relative positions of the two peaks was the opposite of what we observed, i.e., the weaker peak was upfield from the stronger the peak. We compared ^{11}B nmr spectra of BH_3OH^- with that of H_3BNH_3[16] and found that the same trend existed. In other words, the quartet of the hydroxyborohydride ion was at lower field than the quartet of amine borane. This shift in peak position is due to the fact that the boron with the oxygen attached to it is more positive than the boron with the nitrogen attached to it.

As the sample containing the $B_3H_7OH^-$ was warmed above -65° it became apparent that the $B_3H_7OH^-$ was decomposing, giving borate and borohydride. Figure 10 shows a series of spectra recorded approximately two minutes, one-half hour, two hours, and three hours after the sample had been gradually warmed to -28°. Again using the signal due to $B(OH)_{4-x}(OCH_3)_x$ as the reference, the broad signals at ~-10 and +39 ppm are due to the two different kinds of boron in $B_3H_7OH^-$ and the quintet at approximately 45 ppm is the signal of the BH_4^- ion. The very broad signal apparent in the background is the signal due to the boron present in the Pyrex probe insert. We integrated the spectra of Figure 10 over a constant area sufficient to count the nuclei present in the $B(OH)_{4-x}(OCH_3)_x^-$ signal and the signal of B(1) of (I), in order to determine the stoichiometry of the decomposition of $B_3H_7OH^-$. The results of the integration are summarized in Table XII. From Table XII it is seen that the ratio of the change in the area of the $B(OH)_{4-x}(OCH_3)_x$ signal to the change in the area of B(1) of (1) is 1.07. Keeping in mind that B(1) of I is only one-third of the total boron in $B_3H_7OH^-$, the results of the integration indicates that one mole of $B(OH)_4^-$ is produced per mole of $B_3H_7OH^-$ during the decomposition of $B_3H_7OH^-$. The reaction of equation (17) supports this prediction and also agrees with the observation that no hydrogen is produced during the decomposition. Several experiments carried out in vacuo at -30°, revealed that no hydrogen was evolved as $B_3H_7OH^-$ decomposed to BH_4^- and $B(OH)_4^-$.

$$B_3H_7OH^- + 2\ OH^- + H_2O \rightarrow 2\ BH_4^- + B(OH)_4^- \qquad (17)$$

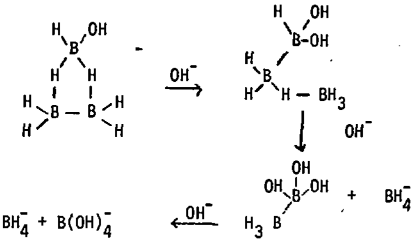
To further prove or disprove that reaction (17) represents the decomposition of $B_3H_7OH^-$, we integrated the area of the BH_4^- and the $B(OH)_{4-x}(OCH_3)_x^-$ signals in spectrum (d) of Figure 10 and found that the ratio of the area of BH_4^- to that of the borate complex was only 1.44 instead of 2.00. This discrepancy is to be expected when the experimental conditions are considered, and the fact that the relaxation time, T_1, of BH_4^- is much longer than T_1 of $B(OH)_4^-$ is taken into account.†

†Errors in integration of data obtained in the pulse Fourier Transform mode can be caused by insufficient spin relaxation (insufficient recovery time between pulses)[17,18] and insufficient acquisition time (the time associated with truncation of the free induction decay, FID). Any manipulation of the data to increase the signal to noise ratio (exponential multiplication of the

FID) will introduce further errors if lines of different widths are to be integrated, as is the case with BH_4^- and $B(OH)_{4-x}(OCH_3)_x^-$ or $B(OH)_4^-$.

In the experiments where the spectra of Figure 10 were recorded, we were interested in following the decomposition of $B_3H_7OH^-$ as a function of time, and aimed for usable signal to noise ratio on the $B(OH)_4^-$ signal, which caused sacrifice of accuracies in the integration, because of the above mentioned reasons.† In a control experiment, a mixture containing an accurately known ratio of BH_4^- to $B(OH)_4^-$ was run under more ideal conditions; the FID was not exponentially multiplied, and both the acquisition and the delay time were increased. The accuracy of the integration determined from the ratio of the areas of the BH_4^- and $B(OH)_4^-$, was consistently better than 2%. Running the same sample under the conditions used while following the decomposition, resulted in integrated areas consistently 30% below the areas expected for BH_4^-. Corrections of the ratio of the integrated areas of BH_4^- and $B(OH)_4^-$ in spectrum (d) of Figure 10 by 30% gives a calculated ratio of 2.06 for the BH_4^- to $B(OH)_4^-$ ratio, which is also consistent with reaction (17).

The following scheme illustrates a possible mechanism of the decomposition of $B_3H_7OH^-$ to two moles of BH_4^- and one mole of $B(OH)_4^-$.



In order to determine if the decomposition was base-catalyzed, we added the same volume of a solution containing $B_3H_7OH^-$ ion to nmr tubes containing NaOH solutions of different concentrations at 0°. The ^{11}B nmr spectra of the mixtures were recorded at 0° in five minute intervals. The spectra are shown in Figure 11. The hydroxide concentration of the various spectra are: (a) and (b), 0.4 M; (c) and (d), 1 M; (e), 2 M and (f), 5 M. As can be seen from Figure 11, no $B_3H_7OH^-$ ion remained in the 5 M NaOH solution, (f), after five minutes at 0°, where as the solution ~0.4 M in hydroxide ion still had an appreciable amount of $B_3H_7OH^-$ after ten minutes. The spectra of Figure 11 indicate that the decomposition of $B_3H_7OH^-$ is base catalyzed.

Since $B_3H_7OH^-$ decomposes in strong base to give BH_4^- and $B(OH)_4^-$ we postulated that its parent compound, $B_3H_8^-$, would undergo a similar decomposition process, also producing BH_4^- and $B(OH)_4^-$. Potassium octahydrotriborate, KB_3H_8, was added to a test tube containing 15 M NaOH, and the tube was placed in an 80° oil bath. As the salt dissolved in the hot NaOH solution, hydrogen was evolved, (evidenced by rapid bubbling of the solution).

After approximately 10 minutes at 80°, the reaction was stopped by placing the test tube in a room temperature water bath. Some of the solution was transferred to an nmr tube and the proton spectrum was recorded. The spectrum was identical to that expected for borohydride, showing four sharp very intense lines with a coupling constant of 27.5 cps and seven less intense with a coupling constant of approximately 80 cps. The reaction was carried out in vacuo in order to determine the amount of hydrogen evolved. In three separate experiments, two at 80° and one at 40° the amount of hydrogen evolved corresponded to 4.12, 4.18, and 4.24 moles of hydrogen per mole of $B_3H_8^-$, respectively. If the decomposition of $B_3H_8^-$ follows the same scheme as that suggested for the decomposition of $B_3H_7OH^-$, the following reaction can be written:

$$B_3H_8^- + 2\ OH^- + 2\ H_2O \longrightarrow 2\ BH_4^- + B(OH)_4^- + 5\ H_2. \qquad (18)$$

If initial attack of hydroxide leads to the formation of $B_3H_7OH^-$, reaction (17) could enter into competition with reaction (18), causing the amount of hydrogen to be less than five moles per $B_3H_8^-$. This being the case, ^{11}B nmr spectra should show that the ratio of the BH_4^- quintet to the borate signal is greater than 0.5 in a completely decomposed $B_3H_8^-$ sample. To check this hypothesis, some KB_3H_8 was placed in an nmr tube with 16 M NaOD and the mixture heated at 75 to 80°. After approximately one hour, the tube was removed from the hot bath and cooled to room temperature, and the ^{11}B nmr spectrum of the solution recorded. The solution contained signals attributable to only BH_4- and $B(OH)_4^-$ but in the ratio of 0.7:1 rather than 0.5:1, indicating that after the formation of $B_3H_7OH^-$, reactions (17) and (18) took place with reaction (18) being dominant.

The rate of hydrogen evolution was followed as a function of time at 50° in 15 and 10 M NaOH. The hydroxide concentration was at least 50 times that of the $B_3H_8^-$ ion, allowing the rate data to be interpreted as those of a pseudo-first-order reaction. The observed rate constant was 2.81×10^{-3} min^{-1} and 9.70×10^{-4} min^{-1} in 15 and 10 M NaOH respectively. The dependence of the observed rate constants on hydroxide ion concentration, prompted us to do an initial-rate study at various concentrations of hydroxide ion at 60°, in order to determine the order of the reaction with respect to hydroxide ion concentration. The results are listed in Table XIII, $X = B_3H_8^-$. A plot of log $\frac{dx}{dt}$ vs. H_- (See Figure 12) is linear but has a slope of only 0.52. The fact that we are using H_- values determined at 25°[19] for studies done at 60° could account for the slope being less than 1. The effect of increasing the temperature becomes more pronounced as the concentration increases, i.e., the acidity function decreases by as much as 0.6 in concentrated H_2SO_4 upon going from 15 to 55°, but remains unchanged in dilute ($\leq$24% by weight) sulfuric acid solutions over the same temperature range. If the effect of temperature on H_- follows the same trend, the slope of the line in Figure 11 would be closer to 1, indicating that the decomposition of $B_3H_8^-$ in strong base is first-order in hydroxide concentration.

Attempts were made to precipitate the $B_3H_7OH^-$ ion by adding to the cold (-78°) solutions a cold (-78°) methanol solution containing tetrabutylammonium iodide. The solutions containing the $B_3H_7OH^-$ ion were checked by ^{11}B nmr before and after adding the $(Bu)_4NI$ solution, and the intensity and the position of the $B_3H_7OH^-$ peaks remained unchanged. Also, the salt that did precipitate out of solution was filtered at -78° and washed with cold 88%

methanol-water. After warming to room temperature the salt was found to be inert to 6 M HCl, indicating that it was probably only $(Bu)_4NCl$ or $(Bu)_4NI$ that precipitated at -78° rather than a boron-hydride species.

Table I. Ratio of hydrogen produced per mole $B_3H_8^-$ at -78° in 88% methanol solutions as a function of hydrogen ion concentration.

$[H^+]$, M	$B_3H_8^-$, mmol	Total amount of H_2, mmol	$H_2/B_3H_8^-$
0.25	2.01	1.94[a]	0.97
1.00	1.10	1.13	1.03
1.25	1.00	0.99	0.99
1.50	1.02	1.05	1.03
2.95	0.70	0.73	1.04
4.02	0.97	1.00	1.03
8.03	1.02	1.10	1.08

[a] Calculated using P value, obtained from a least squares fit of the change in pressure as a function of time, and the ideal gas law, PV = NRT, where v, the volume of the system was known, and T = ambient temperature of the room.

Table II. Ratio of hydrogen produced, in 8 M HCl solutions at -78° during the hydrolysis of $B_3H_8^-$ as a function of percent CH_3OH used.

%v/v CH_3OH	Reaction half-time, hours[a]	H_2 produced[b] at -78°	Total H_2[c] produced	$\frac{H_2 \text{ at } -78^\circ}{H_2 \text{ (total)}}$	
0	0.50	3.01[d]	6.06[d]	0.50[d]	0.01
20	0.60	2.83	5.63	0.50	
36	0.60	3.07	6.05	0.51	
60	0.50	3.76	7.57	0.50	
65	0.42	3.51	6.71	0.52	
70	1.67	2.45	5.43	0.45	

[a] Reaction half-time, defined as time required for evolution of half the total amount of hydrogen evolved at -78°.

[b] Determined by measuring the total amount of hydrogen evolved after waiting 8-12 hours after rate of hydrogen evolution had stopped or become immeasurable.

[c] Determined after warming solutions to room temperature allowing for complete hyrolysis.

[d] Average of nine runs.

Table III. Change in pressure as a function of time for the hydrolysis of $B_3H_8^-$ at $[H^+] = 1.25$ <u>M</u> and at -78°, in 88% methanol-water.

Time, min	Pressure, cm
5	0.17
10	0.36
30	0.99
40	1.27
100	2.71
120	3.07
140	3.41
160	3.77
180	4.00
200	4.25
220	4.49
250	4.86
280	5.04
300	5.15
320	5.27
340	5.34
∞ [a]	6.30

[a] The pressure at infinity was determined from a least squares fit of the data.

Table IV. Effect of acid concentration on the value of the observed pseuo-first-order rate constant at -78^0, for the hydrolysis of KB_3H_8.

$[H^+]$, M	$B_3H_8^-$, M	k_1, $min^{-1} \times 10^3$	k_1', $min^{-1} \times 10^3$
0.20	0.06		0.39[a]
0.25	0.06	0.42[a]	
0.50	0.04		1.61
0.60	0.032	1.81	
0.75	0.032		3.04
1.00	0.034	2.90	3.85
1.25	0.031	3.60	5.62
1.50	0.034		7.04

[a] Calculated using the rate expression,

$$\frac{-d[B_3H_8^-]}{dt} = k_1[B_3H_8^-][H^+] .$$

Table V. The observed rate constants, k_2, as a function of $[H^+]$ for the hydrolysis of $B_3H_7OH_2$ at -45°.

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

[a] Calculated from the rate constant obtained experimentally at -40° and H^+ = 1.25 M, i.e., 4.38×10^{-3} min^{-1}, by assuming that the reaction rate increases by a factor of two for each ten degree rise in temperature.

Table VI. Hydrogen pressure as a function of time for the hydrolysis of $B_3H_7OH_2$ in 3.5 M HCl at -45°.

Time, min	Pressure, cm
5	1.77
15	3.27
20	4.31
30	6.42
40	8.81
50	9.96
60	11.46
70	12.91
80	14.24
90	15.44
100	16.47
120	18.36
140	20.27
160	21.67
180	23.01
200	23.90
220	24.96
240	25.88
260	26.71
285	27.54
300	27.99
330	29.04
360	29.42
390	30.10
420	30.45
450	31.05
480	31.43

Table VII. The calculated rate constants, k_2 and k_3 as a function of hydrogen ion concentration.

$[H^+]$	k_2, min^{-1}	k_2', min^{-1}	k_3, min^{-1} $\underline{M}^{-1}$
0.25	2.92×10^{-3}	2.72×10^{-3}	-1.48×10^{-3}
1.00	3.50×10^{-3}	3.22×10^{-3}	-1.72×10^{-3}
1.25	3.69×10^{-3}	3.28×10^{-3}	-1.68×10^{-3}
1.50	3.64×10^{-3}	2.94×10^{-3}	-2.53×10^{-3}
3.00	7.02×10^{-3}	7.01×10^{-3}	1.04×10^{-5}
3.50	6.89×10^{-3}		6.99×10^{-3}
4.02	6.94×10^{-3}		6.31×10^{-3}
8.03	1.28×10^{-2}		2.16×10^{-1}

Table VIII. Amount of boric acid produced during the hydrolysis of KB_3H_8 in 8 M HCl at -78°, as a function of "dryness".

$\frac{H_a^+}{H_a^+ + H_b^+} = D$	$\frac{\text{mmol } B(OH)_3}{\text{mmol } KB_3H_8}$	
.88	1.45	
.90	1.38	
.91	1.31	
.92	1.29	5%[a]
.93	1.25	3%[b]

[a] Average of 3 experiments.

[b] Average of 5 experiments.

Table IX. Raman Frequency Assignments for the "B_2H_3" solution.[a] Recorded at -78°-80°.

Frequency, cm^{-1}	Assigment
705	BO_3 bending ($B(OH)_3$ or $B(OCH_3)_3$)
800-820	BOC bending
1010	BOH bending and CO stretching
1100-1112	CH_3 rocking
1150	CH_3 bending, symmetric
1460	CH_3 bending. asymmetric
2430	BH
2870-3000 (not shown)	CH stretching, symmetric and asymmetric
3200 (not shown)	OH stretching

[a] Solvent - 20% methanol - water.

Table X. Hydrogen Pressure as a Function of time for $[H^+]$ = 8 M at -78°, for the hydrolysis of $B_3H_8^-$.

$[B_3H_8^-]$ = 0.015, 0% CH_3OH		$[B_3H_8^-]$ = 0.013, 70% CH_3OH	
Time, min	Pressure, cm	Time, min	Pressure,cm
4	6.81	3	6.39
10	8.85	8	6.57
15	9.12	13	7.15
20	10.27	20	7.78
25	11.26	25	8.14
30	12.19	30	8.61
35	13.13	40	9.39
40	13.19	50	10.23
50	15.48	60	10.98
60	16.99	80	12.52
80	19.37	100	13.85
100	21.07	120	14.90
120	22.44	140	15.89
140	23.28	160	16.86
160	23.96	180	17.61
180	24.52	200	18.55
220	25.31	220	19.31
240	25.55	240	19.85
260	25.77	270	20.65
280	25.91	300	20.85
300	26.03	330	21.56
330	26.19	360	22.11
		390	22.58
		420	22.96
		480	23.53
		510	23.77
		600	23.98
		630	24.11
		660	24.76
		690	24.37
		720	24.48
		840	24.57
		900	24.66
		1012	24.87
		1115	25.01
		1280	25.04
		1400	25.17

Table XI. Hydrogen Pressure as a Function of time for $[H^+]$ = 8 M, $[CH_3OH]$ = 70% v/v -36°, hydrolysis of unknown species.

Pressure, cm	Time, min
2.01	0
3.77	5
5.62	10
7.30	15
8.94	20
10.34	25
13.06	35
15.10	45
16.68	55
19.25	75
20.59	95
22.10	115
22.98	135
23.76	155
24.24	195
25.08	215
25.70	235
26.01	255
26.27	275
26.70	295
27.50	375
27.60	405
27.90	440
28.39	480
28.48	510

Table XII. The integrated area[a] of the spectra of Figure 10.

SPECTRUM	Integrated area of B(1)	Integrated area of $B(OH)_{4-x}(OCH_3)_x$
(a)	86.76	13.24
(b)	43.28	56.72
(c)	14.39	85.61

[a] The constant integral integrated was from -17.23 to +2.28 ppm ($B(OH)_{4-x}(OCH_3)_x$ = 0).

Table XIII. Initial rates, dx/dt, of the decomposition of KB_3H_8[a] at 60° as a function of $[OH^-]$. x = KB_3H_8

OH^-, M	dx/dt, $sec^{-1} \times 10^3$	H-
5	0.88	15.20
6	1.21	15.40
7	1.43	15.62
8	1.94	15.75
9	2.50	15.97
10	3.31	16.20
11	4.00	16.42
12	5.52	16.58
13	6.37	16.76
14	7.70	16.93
16	12.50	17.30

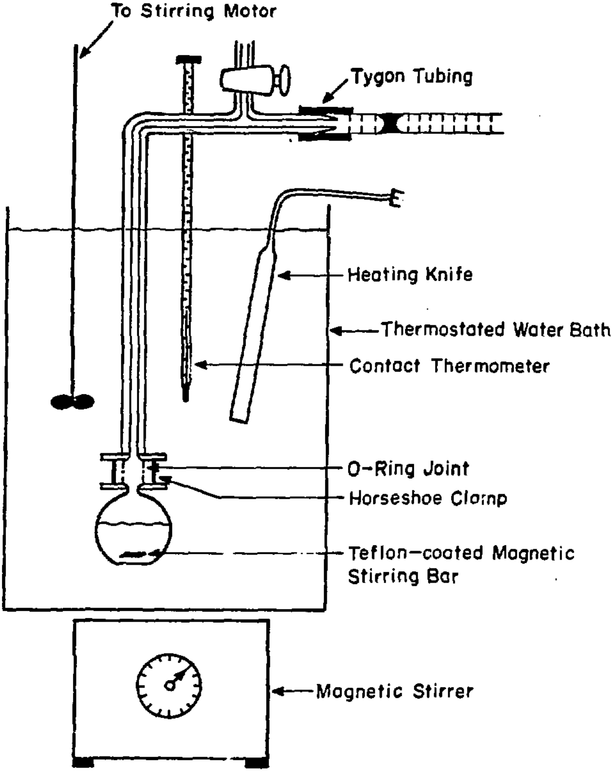
Figure Captions

1. Reaction set up used for initial rate studies.
2. Reaction vessels used to determine stoichiometry of $B(OH)_3$ produced during the reaction of KB_3H_8 with 8 M HCl at -78.
3. Semi-logarithmic plot of $(P_\infty - P)$ versus time for the hydrolysis of KB_3H_8 in $[H^+] = 1.25$ M at -78°, in 88% methanol-water.
4. Plot of observed rate constants versus hydrogen ion concentration for the hydrolysis of KB_3H_8 at -78°.
5. Semi-logarithmetic plot of $(P_\infty - P)$ versus time for the hydrolysis of $B_3H_7OH_2^-$ in $[H^+] = 1.25$ M and at -45°.
6. Plot of $1/(P_\infty - P_t)$ versus time for the hydrolysis of $B_3H_7OH_2$ ion 4 M HCl at -45°.
7. Plot of $B(OH)_3/KB_3H_8$ versus "dryness".
8. Raman Spectrum of a solution containing the unknown boronhydride species produced during the hydrolysis of $B_3H_8^-$ at -78° in 8 M HCl containing 20% methanol by volume.
9. ^{11}B nmr spectrum of $B_3H_7OH^-$ solution recorded at -55°.
10. ^{11}B nmr spectra showing the decomposition of $B_3H_7OH^-$ as a function of time at -28°. (a), t = 2 minutes; (b), t = 30 minutes; (c), t = 2 hours; (d), t = 3 hours.
11. ^{11}B nmr spectra recorded at 0°, illustrating the base catalized decomposition of $B_3H_7OH^-$.
    - (a) Spectrum of $B_3H_7OH^-$ as prepared, $[OH^-] = 0.4$ M, after being at 0° for five minutes;
    - (b) Same as (a), five minutes later.
    - (c) $B_3H_7OH^-$ in 1 M NaOH after being at 0° for five minutes.
    - (d) Same as (c), five minutes later.
    - (e) $B_3H_7OH^-$ in 2 M NaOH after being at 0° for five minutes.

(f) $B_3H_7OH^-$ in 5 M NaOH after being at 0° for five minutes.

(g) The $B(OH)_{4-x}(OCH_3)_x^-$ signal expanded (in order to show splitting) is shown in the insert of (a).

12. Plot of log(dx/dt) versus H- for the decompositon of $B_3H_8^-$ in strong base at 60°, where X = $B_3H_8^-$.



XBL 7710-6189

Fig. 1

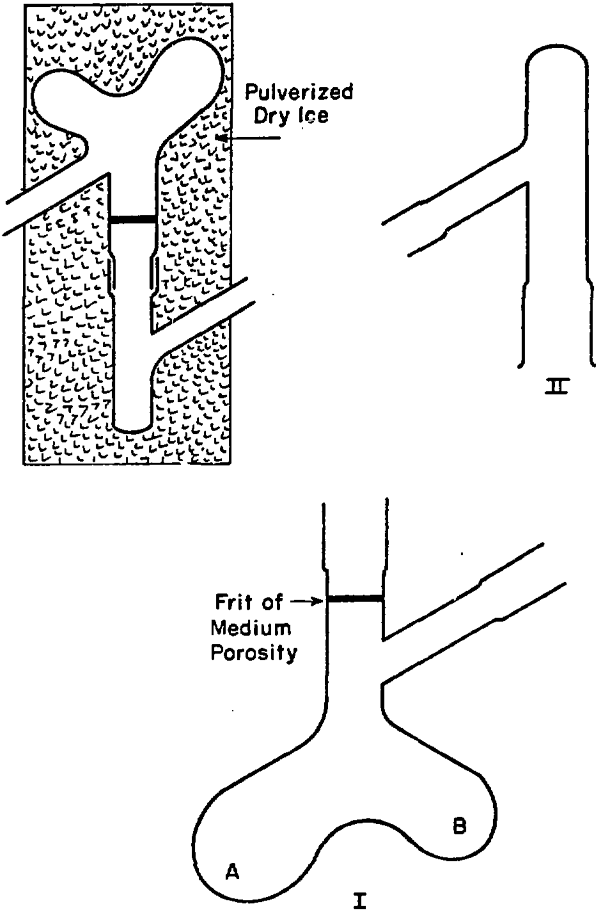


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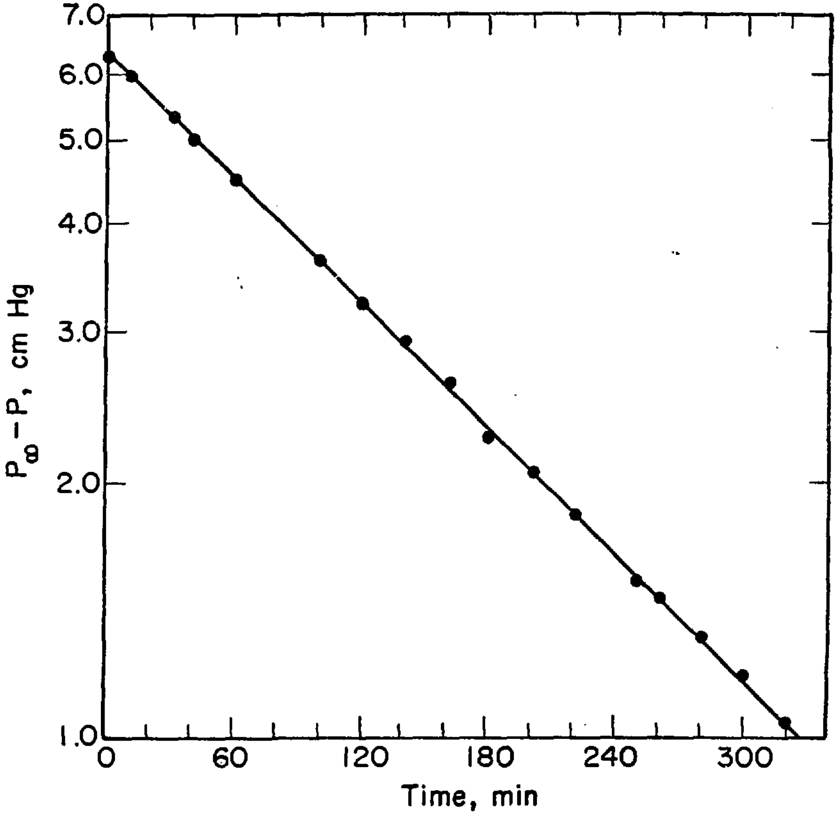
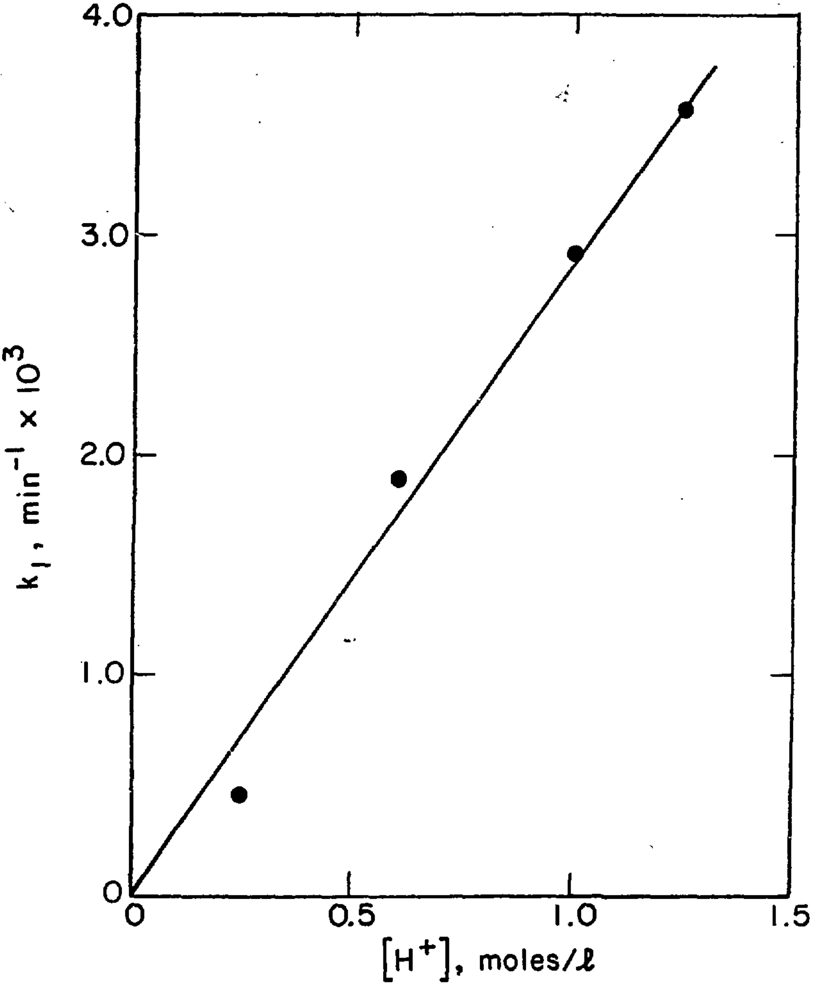
Fig. 2



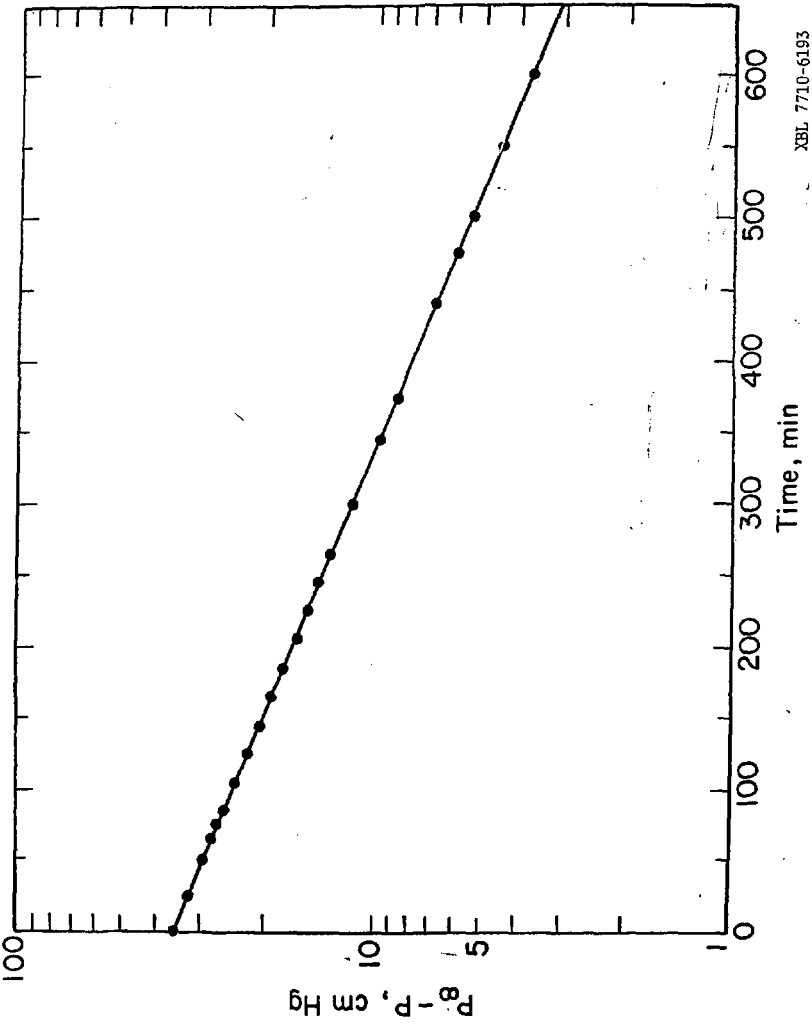
XBL 7710-6191

Fig. 3



XBL 7710-6192

Fig. 4



XBL 7710-6193

Fig. 5

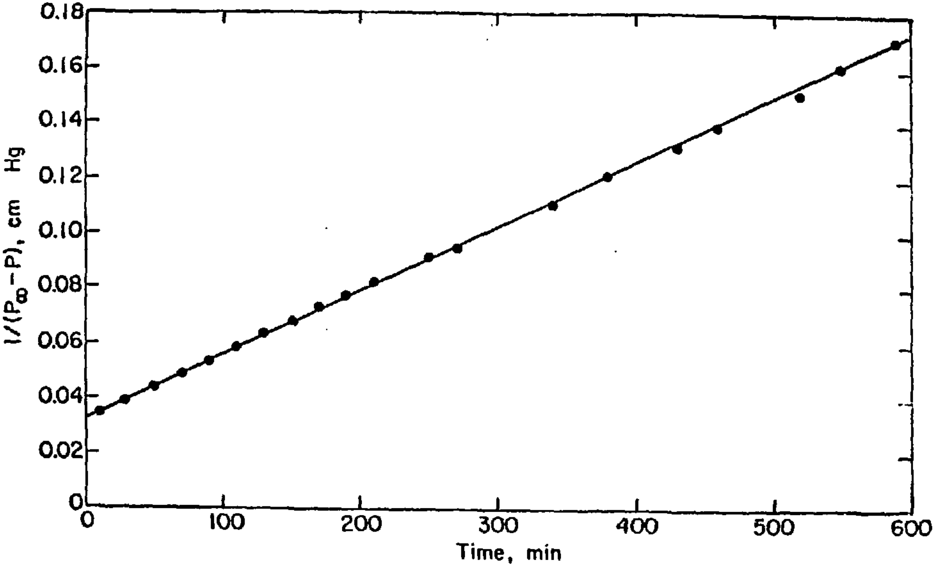
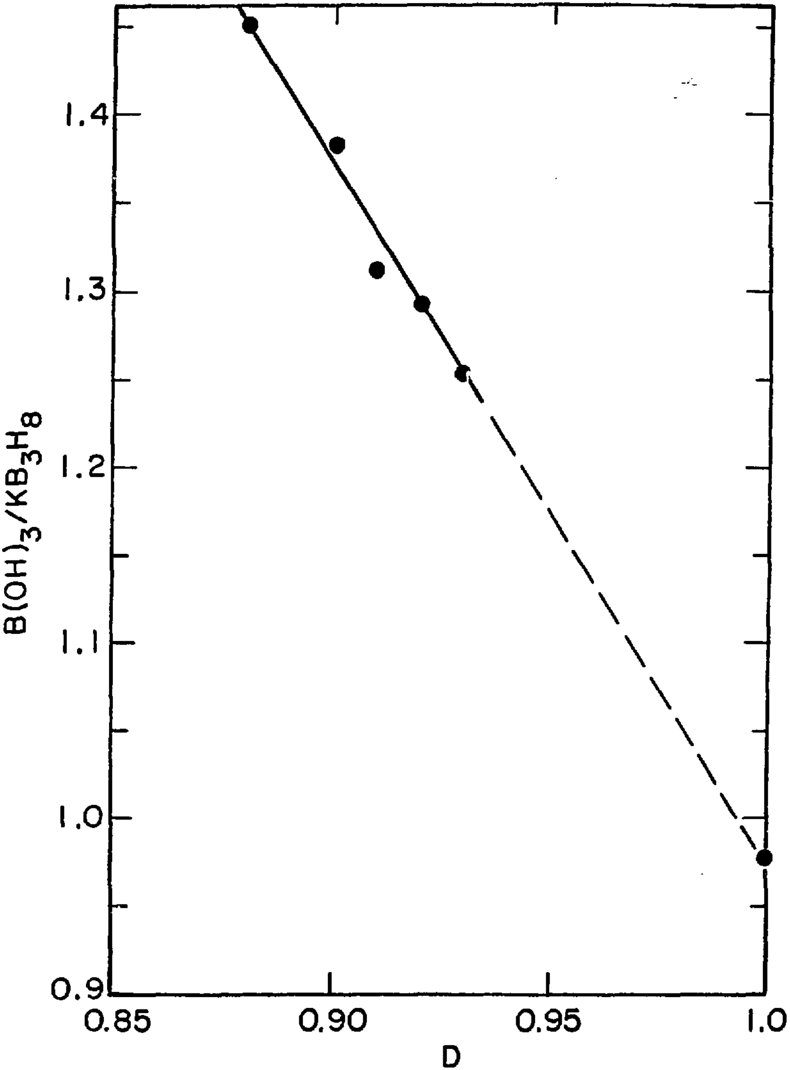


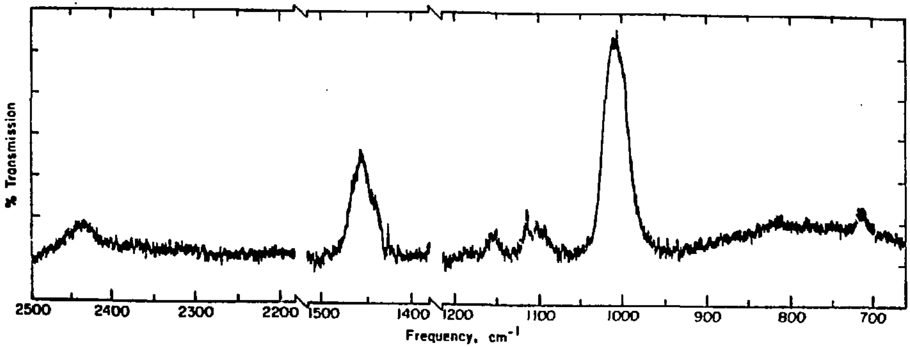
Fig. 6

XBL 7710-6194



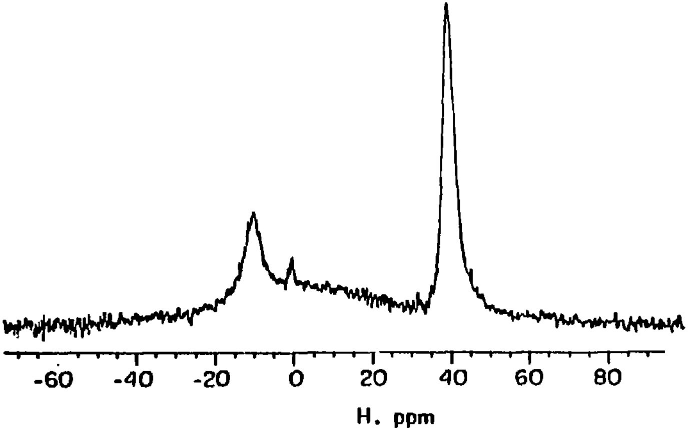
XBL 7710-6195

Fig. 7



XBL 7710-6196

Fig. 8



XBL 7710-6197

Fig. 9

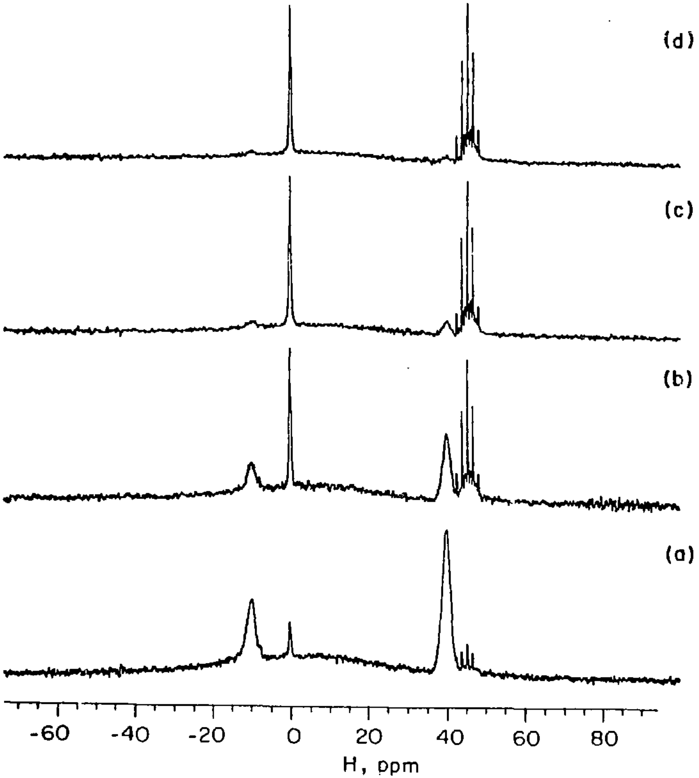


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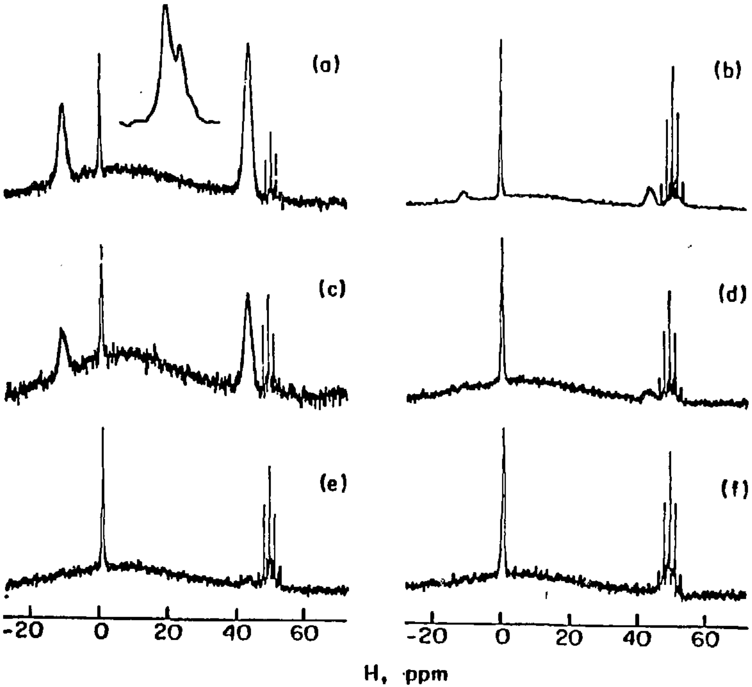
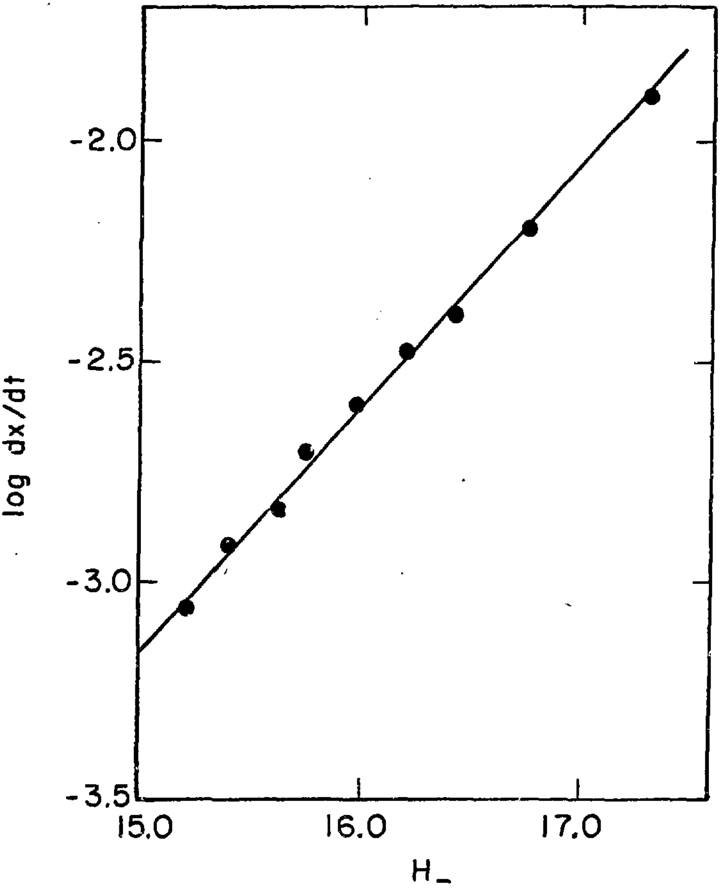
Fig. 10



XBL 7710-6199

Fig. 11



XBL 7710-6200

Fig. 12

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