Evidence for BH₂⁺ in Cold Acidic Solutions

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Potassium hydroborate reacts with 8 M HCl at $-70°$ to form 2 moles of hydrogen/mole of hydroborate and a solution which yields another 2 moles of hydrogen when warmed above $-20°$. Diborane reacts slowly with 8 M HCl at $-75°$ to form 2 moles of hydrogen/mole of diborane; 4 more moles of hydrogen is evolved upon warming the solution above $-20°$. These and other data suggest that, in both reactions, the aquated BH₂⁺ ion is formed at the low temperature.

Introduction

We recently reported[1] that diborane and hydroborates react with aqueous acids at temperatures near $-70°$ to form strongly reducing solutions. The formation of the aquated BH_2^+ ion was postulated.

$$B_2H_6 + 2H^+ + 4H_2O \longrightarrow 2(H_2O)_2BH_2^+ + 2H_2$$

$$BH_4^- + 2H^+ + 2H_2O \longrightarrow (H_2O)_2BH_2^+ + 2H_2$$

In this paper we present experimental data and arguments supporting these reactions.

Experimental Section

Potassium hydroborate was obtained from Metal Hydrides, Inc., Beverly, Mass. Diborane was prepared by adding potassium hydroborate to phosphoric acid.[2] When required, standard vacuum-line manipulation was used.

Large-Scale Reaction of KBH₄ with HCl[3].—A 1-l. four-necked flask was equipped with a nitrogen inlet tube, a stirrer, a thermometer, and an addition tube containing 16 g of potassium hydroborate. Aqueous 7.8 M HCl (200 ml) was added to the flask and cooled to ca $-70°$ with a Dry Ice-acetone bath. The potassium hydroborate was slowly added to the acid, keeping the temperature of the solution below $-60°$ at all times. Cold nitrogen was blown over the solution during the hydroborate addition. When all of the hydroborate had been added, the stirring and cold nitrogen flow were continued until about half the solution was frozen. The mixture was then filtered through a sintered-glass filter in a $-70°$ bath. The filtrate contained the reducing species in concentrations of 1.3–2.0 N, as determined either by titration with a cold iodine solution or by measurement of the hydrogen evolved upon warming to room temperature.

Nmr Studies.[3]—Attempts to obtain proton magnetic resonance spectra of the cold solutions prepared as described above were made using a Varian A-60 spectrometer equipped with a sample cavity cooled to -50 to $-60°$. No signal other than that of the solvent was ever observed. Even when solutions prepared in methanol–aqueous HCl mixtures (to reduce viscosity) and in D_2O–DCl solutions (to reduce the solvent signal) were examined, no novel signals were ever observed. Similarly, while any of the above solutions were being warmed to room temperature (with decomposition), no novel signals were observed. Boron-11 nmr spectra of the solutions prepared as described above were obtained using a Varian variable-frequency (VF-16) instrument equipped with a sample cavity cooled to $-45°$. Although there was some effervescence of the sample, operation at this temperature was tolerable because the signal intensity did not diminish rapidly with time, and the peak intensity was found to increase with increasing temperature (probably a viscosity effect). The solutions showed a very broad peak centered 28.8 $\pm$ 2 ppm

upfield from the signal of BCl_3. After allowing such a solution to decompose at room temperature, the spectrum was run again at $-45°$ and showed a broad peak at 22.5 $\pm$ 2 ppm upfield from BCl_3. In a separate experiment, a solution of boric acid in the same solvent was shown to yield a peak at 21.6 $\pm$ 2 ppm upfield from BCl_3.

Attempt to Prepare [(CH₃)₃N]₂BH₂⁺.[3]—An acidic reducing solution was prepared as described above, except that 7.8 M HCl which had been prepared from aqueous 12 M HCl and methanol was used as the solvent. The solution was slowly titrated with 8 M methanolic KOH, while maintaining the temperature of the main solution below $-50°$. Gaseous trimethylamine was passed into the neutralized solution for 10 min; the solution was warmed to room temperature and filtered from the voluminous precipitate (principally KCl) which formed. One portion of the filtrate was evaporated to half its volume, filtered, and extracted with methylene chloride. Evaporation of the extract yielded a solid whose infrared spectrum was quite unlike that of a sample of [(CH₃)₃N]₂-BH₂⁺I⁻. Specifically, a band characteristic of the B–H stretching vibration was absent from the unknown spectrum. Another portion of the filtrate was evaporated to dryness and then extracted with methylene chloride. The residue obtained after drying the solvent and evaporation to dryness had an infrared spectrum with no B–H band.

Attempted Extraction with Ether.[3]—A freshly prepared reducing solution (prepared as described above) was shaken with cold diethyl ether. When a few drops of an iodine–ether solution was added to the separated ether layer, the iodine color did not disappear, indicating the absence of reducing agent in the ether.

Quantitative Studies with KBH₄.—In three separate experiments, 0.01–0.02 g of KBH₄ was added to about 9 ml of aqueous 8 M HCl at $-78°$ in an evacuated reaction vessel. The mixture was magnetically stirred for about 1.5 hr, after which a clear solution remained. The evolved hydrogen was determined. The solution was then warmed to room temperature, and when effervescence of the solution ceased, the evolved hydrogen was determined. For the three experiments, the ratios of initial hydrogen to total hydrogen were 0.490, 0.505, and 0.510.

In another experiment, 0.5 g of KBH₄ was added during a period of 1.5 hr to 10 ml of magnetically stirred aqueous 8 M HCl at $-78°$ while pumping the evolved gases through a $-78°$ trap and two $-196°$ traps. The $-196°$ traps collected 0.10 mmole of B_2H_6 (identified by its infrared spectrum), corresponding to a 2% yield.

Quantitative Studies of B₂H₆.—In three separate experiments, 0.3–0.6 mmole of diborane was introduced to a vertical cylindrical reaction vessel (38 × 300 mm) containing about 10 ml of magnetically stirred aqueous 8 M HCl in the bottom of the vessel, cooled to $-78°$. About 8 cm² of the HCl solution was exposed to the gas. In each case, after a period of 2–3 hr, only about half of the diborane was consumed. The evolved hydrogen and unconsumed diborane were pumped out, and the hydrogen was measured. The reaction vessel was then warmed to about 20°, where hydrogen was evolved vigorously. After about 20 min, the hydrogen was determined. (In a separate experiment, it was determined that all of the hydrogen was evolved in a period of 2

(1) W. L. Jolly and T. Schmitt, *J. Am. Chem. Soc.*, **88**, 4282 (1966).

(2) B. J. Duke, J. R. Gilbert, and I. A. Read, *J. Chem. Soc.*, 540 (1964).

(3) For further experimental details, see T. Schmitt, M.S. Thesis, University of California, Berkeley, Calif., Jan 1966; University of California Radiation Laboratory Report UCRL-16659.

min or less.) For the three experiments, the ratios of initial hydrogen to total hydrogen were 0.34, 0.34, and 0.35.

In two separate experiments, similar in procedure and apparatus to those described immediately above, diborane was allowed to react with 5.4 M HClO$_4$ at approximately $-55°$. Again the diborane reacted incompletely, and again the solutions effervesced when warmed to room temperature. For the two experiments, the ratios of initial hydrogen to total hydrogen were 0.45 and 0.36.

In another set of experiments, similar to those described above, diborane was allowed to react with dilute solutions of HCl in water-ethanol solutions (approximately 12% H$_2$O, 88% C$_2$H$_5$OH) at $-78°$. In these experiments the diborane appeared to be completely consumed (as evidenced by the cessation of bubbling) in about 30 min; however, the reaction mixtures were allowed to stand for 1 or 2 hr to ensure complete reaction. When the reaction vessel was warmed to 20°, hydrogen was evolved relatively slowly; a half-time of about 2 min was observed in one experiment with 0.24 M HCl. It was therefore necessary to hold the solutions for about 1 hr at room temperature before measuring the total evolved hydrogen. In five experiments with 0.24 M HCl, the ratios of initial hydrogen to total hydrogen were 0.35, 0.35, 0.35, 0.36, and 0.36. In an experiment with 1.2 M HCl, the ratio was 0.34.

In two experiments at $-78°$ with 0.24 M HCl in 12% H$_2$O-88% C$_2$H$_5$OH, an excess of coarsely ground particles of KOH was slowly added to the solution after measurement of the hydrogen evolved in the initial reaction of the diborane. In one experiment, 0.30 g of KOH was added; after stirring for 4.5 hr, the evolved hydrogen was determined and found to equal 98.5% of the amount evolved in the initial reaction of the diborane. After stirring for another hour, only a trace of hydrogen was evolved. In the other experiment, 0.35 g of KOH was added; after stirring for 4 hr, the evolved hydrogen was determined to be 85% of that evolved in the initial reaction of the diborane. No detectable hydrogen was evolved upon stirring for a further 3 hr. (In this latter experiment, the initial hydrogen evolved was probably too high because of inadequate cooling by the Dry Ice bath. The sum of the initial and secondary amounts of hydrogen amounted to 3.95 moles of H$_2$/mole of B$_2$H$_6$ consumed.) In both experiments, the resulting basic solutions had the characteristics of solutions containing BH(OH)$_3$$^-$ ions.[1,4]

Experiment with P(CH$_3$)$_3$.—Diborane (0.402 mmole out of 0.609 mmole) reacted with a mixture of 2 ml of ethanol and 8 ml of aqueous 8 M HCl at $-78°$, with evolution of 0.830 mmole of hydrogen. The solution was then treated with 1.04 mmoles of trimethylphosphine (prepared by the method of Mann and Wells[5]). The stirred solution was held at $-78°$ for 5 hr and then slowly warmed to room temperature. A total of 2.43 mmoles of hydrogen was evolved (6.05 moles/mole of consumed B$_2$H$_6$), indicating that no significant amount of [(CH$_3$)$_3$P]$_2$BH$_2$$^+$ had formed. The trimethylphosphine was recovered as the hydrochloride by evaporating the solution.

Discussion

We here enumerate the conclusions which we have drawn regarding the nature of the species formed in the reactions of hydroborate and diborane with cold aqueous acid.

(1) The reducing species probably contains boron because the reducing solution gave a boron-11 nmr signal which disappeared as the species decomposed and which was replaced by a signal due to boric acid.

(2) We believe that only one reducing species is formed in the reaction of hydroborate with cold 8 M HCl and that only one reducing species is formed in the reaction of diborane with cold 8 M HCl. We draw

(4) W. L. Jolly, unpublished observations, 1966.

(5) F. G. Mann and A. F. Wells, *J. Chem. Soc.*, 702 (1938).

these conclusions because, in all of our quantitative studies of these reactions, close to an integral number of moles of hydrogen was evolved per mole of reactant. Only fortuitously could two or more concurrent reactions consistently have yielded these unique results.

(3) It seems likely that the same reducing species is formed in both the hydroborate and diborane reactions, because both reactions yield solutions containing four equivalents of reducing power per boron atom.

(4) Hydrochloric acid (or chloride ion) does not have a specific influence on the course of the diborane reaction, as shown by the fact that cold perchloric acid gives similar results. In the experiments with perchloric acid, somewhat more hydrogen was evolved than in the experiments with hydrochloric acid (2.70 and 2.16 moles of H$_2$/mole of B$_2$H$_6$ in 5.4 M HClO$_4$, as opposed to 2.04, 2.04, and 2.10 moles of H$_2$/mole of B$_2$H$_6$ in 8 M HCl). We believe that the principal reaction was the same in both sets of experiments, but that some extra hydrolysis occurred in the HClO$_4$ experiments because these experiments were carried out at a temperature about 20° higher. (The eutectic temperature of aqueous HClO$_4$ is higher than that of aqueous HCl.)

(5) Various structures are consistent with the above conclusions. These include the four possible diborane-like structures (such as H$_2$B(OH)$_2$BH$_2$), aquated hydroxyborane, H$_2$OBH$_2$OH, and aquated boranium ion, (H$_2$O)$_2$BH$_2$$^+$. The diborane-like structures seem unlikely to us because many other studies have shown that diborane always reacts with polar solvents such as water to form monoboron fragments.[6–8] Of the two monoboron species which we have considered, we prefer the ionic species, (H$_2$O)$_2$BH$_2$$^+$, because other studies indicate that the neutral species, H$_2$OBH$_2$OH, is hydrolytically unstable with respect to H$_2$OBH(OH)$_2$ even at low temperatures.[9,10] We believe that, in acidic solutions, aquated hydroxyborane is protonated to give (H$_2$O)$_2$BH$_2$$^+$ and that this protonated species is relatively inert toward hydrolysis.[11] Many boranium ions of the general formula (base)$_2$BH$_2$$^+$ are known, and in the cases where the base is an amine, the ions are remarkably stable toward hydrolysis. Resistance toward hydrolysis decreases with decreasing basicity of the co-

(6) R. A. Geanangel and S. G. Shore in "Preparative Inorganic Reactions," Vol. 3, W. L. Jolly, Ed., Interscience Publishers, Inc., New York, N. Y., 1967, Chapter 4; H. I. Schlesinger and A. B. Burg, *Chem. Rev.*, **31**, 1 (1942); F. G. A. Stone, *Advan. Inorg. Chem. Radiochem.*, **2**, 279 (1960).

(7) G. E. McAchran and S. G. Shore, *Inorg. Chem.*, **4**, 125 (1965).

(8) S. G. Shore, C. W. Hickam, Jr., and D. Cowles, *J. Am. Chem. Soc.*, **87**, 2755 (1965).

(9) When diborane is allowed to react with ethanol-water solutions[1] at $-75°$, or with ice[10] at $-80°$, 4 moles of hydrogen is evolved per mole of diborane. We believe that, in these reactions, aquated hydroxyborane is formed as an intermediate, but that it immediately hydrolyzes to aquated dihydroxyborane: H$_2$OBH$_2$(OH) + H$_2$O → H$_2$OBH(OH)$_2$ + H$_2$. Apparently this latter hydrolysis is suppressed in the acidic solutions of the present investigation.

(10) H. G. Weiss and I. Shapiro, *J. Am. Chem. Soc.*, **75**, 1221 (1953).

(11) In the rate-determining step of the hydrolysis, a B–H bond is broken. In order to maintain the tetracovalency of the boron, the bond order of the B–O bonds would be expected to increase. This partial double-bond formation (involving a shift in electron density from oxygen to boron) would be expected to be less favored when both oxygens are bonded to two hydrogens than when one of them is bonded to only one hydrogen.

ordinated base,[12] and the susceptibility toward hydrolysis which we observe for our reducing species is that expected for a $(H_2O)_2BH_2^+$ species. The ionic formulation for the reducing species is consistent with our inability to extract it into ether.

According to the above postulates, a cold acidic solution of $(H_2O)_2BH_2^+$, when neutralized with base, should evolve 1 mole of hydrogen/mole of $(H_2O)_2BH_2^+$, corresponding to hydrolysis to $H_2OBH(OH)_2$. This was proven to be the case in two experiments.

Unsolved Problems.—The extremely broad, featureless boron-11 nmr spectrum of the reducing species was very disappointing. McAchran and Shore[7] were unable to observe a well-defined spectrum of the $((CH_3)_2SO)_2BH_2^+$ ion, and Schaeffer, Tebbe, and Phillips[13] only observed a very broad $(dioxane)_2BH_2^+$ signal. Apparently B^{11} quadrupole relaxation can be significant in ions of this type.[8] Boron-11 quadrupole relaxation also was probably responsible for our inability to see a proton nmr signal. Possibly B^{11} double-resonance experiments would be fruitful.

(12) N. E. Miller and E. L. Muetterties, *J. Am. Chem. Soc.*, **86**, 1033 (1964).
(13) R. Schaeffer, F. Tebbe, and C. Phillips, *Inorg. Chem.*, **3**, 1475 (1964).

In our attempt to convert $(H_2O)_2BH_2^+$ to $[(CH_3)_3N]_2BH_2^+$, we necessarily neutralized the solution. According to our ideas regarding the relative stabilities of $(H_2O)_2BH_2^+$ and H_2OBH_2OH (expressed above), this neutralization caused deprotonation and hydrolysis of the reducing species. Our attempt to convert $(H_2O)_2BH_2^+$ to $[(CH_3)_3P]_2BH_2^+$ was unsuccessful probably because the trimethylphosphine was protonated in the acidic solution. It might be more worthwhile to attempt precipitation of insoluble salts of the $(H_2O)_2BH_2^+$ cation.

We were surprised to find that diborane reacts very slowly with cold aqueous acid. Under conditions such that diborane would react completely with an ethanol-water solution in about 20 min, diborane was only half-reacted with 8 M HCl in 3 hr. We can only surmise that the rate-determining step for the hydrolysis involves the attack of water and that the activity of water was so low in the acidic solutions as to reduce the rate significantly.

Neutron-Scattering Study of the Motions of Water Molecules in Hydrated Salts of Transition Metals[1]

By J. J. Rush,[2] J. R. Ferraro,[3] and A. Walker[3]

The low-frequency motions of water molecules in a series of hydrated transition metal salts have been investigated by the energy-gain scattering of cold neutrons. The compounds studied include $CuSO_4 \cdot H_2O$, $CuSO_4 \cdot 5H_2O$, $Co(NO_3)_2 \cdot 2H_2O$, $Co(NO_3)_2 \cdot 6H_2O$, $Cu(NO_3)_2 \cdot 3H_2O$, and $UO_2(NO_3)_2 \cdot 6H_2O$. Broad bands observed in the spectra at neutron energy gains of 500–800 cm^{-1} are assigned to the wagging and rocking modes of the coordinated and hydrogen-bonded water molecules. Bands around 400–500 cm^{-1} are attributed both to M–OH_2 stretching modes and to the H_2O torsional vibrations around the bisectrix. Maxima are also observed at energy transfers below 300 cm^{-1}, which are tentatively assigned to hydrogen-bond stretching vibrations and possibly to H_2O–M–OH_2 deformation modes. Comparison of the various spectra appears to indicate that the average strength of binding of the water molecules does not change significantly in proceeding from the higher to the lower hydrates. The neutron results are compared in detail with previous infrared and structure results.

I. Introduction

Recent infrared spectra from 4000 to 70 cm^{-1} on a series of anhydrous and hydrated transition metal salts have provided considerable information concerning the coordination of anion groups and water molecules to the metal atoms.[4–6] In particular, the spectra indicate the existence of relatively strong metal–oxygen bonds to nitrate and sulfate anions in the anhydrous

and lower hydrate salts. Low-frequency bands in the region 250–400 cm^{-1} have been assigned to the M–O stretching vibrations. These bands do not appear in the spectra for the penta- and hexahydrates, presumably because more water molecules enter the coordination sphere, and the anion groups move further away from the metal atoms. Other peaks in the infrared spectra of the hydrates in the region from 400 to 900 cm^{-1} have been attributed to M–OH_2 stretching modes of the coordinated water molecules, as well as to H_2O librations. The low-frequency motions of water molecules in these and other complex solids are many times difficult to observe or assign, however, owing to weak or

(1) Work supported by the U. S. Atomic Energy Commission.
(2) Argonne National Laboratory and National Bureau of Standards; address inquiries to this author at National Bureau of Standards.
(3) Argonne National Laboratory.
(4) J. R. Ferraro and A. Walker, *J. Chem. Phys.*, **42**, 1273, 1279 (1965).
(5) J. R. Ferraro and A. Walker, *ibid.*, **43**, 2689 (1965).
(6) J. R. Ferraro and A. Walker, *ibid.*, **45**, 550 (1966).