UCRL-17280

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Berkeley, California

Submitted to Inorganic Chemistry

UCRL-17280
Preprint

UNIVERSITY OF CALIFORNIA

Lawrence Radiation Laboratory
Berkeley, California

AEC Contract W-7405-eng-48

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William L. Jolly and Theresa Schmitt

September 1966

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UCRL-17280

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

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William L. Jolly and Theresa Schmitt

Abstract

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 are evolved upon warming the solution above -20°. These and other data suggest that, in both reactions, the aquated BH_2^+ ion is being formed at the low temperature.

Introduction

It has generally been assumed that hydridic reagents such as hydroborates and diborane would be completely hydrolyzed in a strongly acidic solution such as 8 M HCl, no matter how cold the solution. Thus it was entirely accidentally that we found that a kinetically stable intermediate can be prepared quantitatively by these reactions.[1] A brief outline of the events leading to this discovery follows.

When stannane is prepared (in low yield) by slowly dropping an alkaline solution of stannite and hydroborate into ice-cold hydrochloric acid,[2] each drop causes the formation of a bright yellow precipitate which rapidly turns grey. We found that it is possible to stabilize the yellow material by adding the stannite-hydroborate solution to 8 M HCl cooled to -70°.[3] When the yellow suspension was warmed to room temperature, it darkened, and hydrogen was evolved. But, to our amazement, the amount of evolved hydrogen was too great to be explicable in terms of any reasonable tin compound. We soon learned that the stannite had nothing to do with the hydrogen evolution. When stannite was omitted from the added solution, no yellow precipitate formed; but the resulting solution could be titrated with iodine, and it liberated hydrogen when warmed to temperatures above -20°. It then seems likely to us that some sort of strongly reducing boron compound was being formed. We found that when diborane reacts with 8 M HCl at -70°, the resulting solution has the same properties as those solutions formed by the reaction of hydroborate.

In this paper we describe various experiments which have a bearing on the nature of these cold reducing solutions.

Experimental Section

General. - Potassium hydroborate was obtained from Metal Hydrides, Inc., Beverly, Massachusetts. Diborane was prepared by adding potassium hydroborate to phosphoric acid.[4] When required, standard vacuum-line manipulation was used.[5]

Large Scale Reaction of KBH_4 with HCl.[3] - A 1-liter, 4-necked flask was equipped with a nitrogen inlet tube, a stirrer, a thermometer, and an addition tube containing 16 g. of potassium hydroborate. Two hundred ml. of 7.8 M HCl 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 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 to 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.

N.M.R. 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 ± 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 ± 2 ppm upfield of BCl_3. In a separate experiment, a solution of boric acid in the same solvent was shown to yield a peak at 21.6 ± 2 ppm upfield of BCl_3.

Attempt to Prepare $[(CH_3)_3N]_2BH_2^+$.[3] - An acidic reducing solution was prepared as described above, except that 7.8 M HCl which had been prepared from 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 minutes; 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 one-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 $[(CH_3)_3N]_2BH_2^+I^-$. 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 KBH_4. - In three separate experiments, 0.01-0.02 g. of KBH_4 was added to about 9 ml. of 8 M HCl at -78° in an evacuated reaction vessel. The mixture was magnetically stirred for about 1.5 hr., after which time 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/total hydrogen were 0.490, 0.505, and 0.510.

In another experiment, 0.5 g. of KBH_4 was added during a period of 1.5 hr. to 10 ml. of magnetically stirred 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 with B_2H_6. - In three separate experiments, 0.3 - 0.6 mmole of diborane was introduced to a vertical cylindrical reaction vessel (38 x 300 mm) containing about 10 ml. of magnetically stirred 8 M HCl in the bottom of the vessel, cooled to -78°. About 8 sq. cm. of the HCl solution was exposed to the gas. In each case, after a period of 2-3 hrs., only about one-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°, at which temperature hydrogen was evolved vigorously. After about 20 minutes, the hydrogen was determined. (In a separate experiment, it was determined that all the hydrogen was evolved in a period of two minutes or less.) For the three experiments, the ratios of initial hydrogen/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 imcompletely, and again the solutions effervesced when warmed to room temperature. For the two experiments, the ratios of initial hydrogen/ 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_2O, 88% EtOH) at -78°. In these experiments the diborane appeared to be completely consumed

(as evidenced by the cessation of bubbling) in about 30 minutes; however the reaction mixtures were allowed to stand for one or two hours to ensure complete reaction. When the reaction vessel was warmed to 20°, hydrogen was evolved relatively slowly; a half-time of about 2 minutes was observed in one experiment with 0.24 M HCl. It was therefore necessary to hold the solutions for about an hour at room temperature before measuring the total evolved hydrogen. In five experiments with 0.24 M HCl, the ratios of initial hydrogen/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_2O-88% EtOH, 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. KOH was added; after stirring for 4.5 hours, 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 hours, 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 three hours. (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_2H_6 consumed.) In both experiments, the resulting basic solutions had the characteristics of solutions containing $BH(OH)_3^-$ ions.[1,6]

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 these conclusions because, in all 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_2H_6 in 5.4 M $HClO_4$, as opposed to 2.04, 2.04 and 2.10 moles of H_2/mole of B_2H_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 $H_2B(OH)_2BH_2$), aquated hydroxyborane, H_2OBH_2OH, and aquated boranium ion, $(H_2O)_2BH_2^+$. 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. Of the two monoboron species which we have considered, we prefer the ionic species, $(H_2O)_2BH_2^+$, because other studies indicate that the neutral species, H_2OBH_2OH, is hydrolytically unstable with respect to $H_2OBH(OH)_2$ even at low temperatures.[7] We believe that, in acidic solutions, aquated hydroxyborane is protonated to give $(H_2O)_2BH_2^+$, and that this protonated species is relatively inert toward hydrolysis.[9] Many boranium ions of the general formula $(base)_2BH_2^+$ 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 coordinated base,[10] 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 one mole of hydrogen per 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[11] were unable to observe a well-defined spectrum of the $(Me_2SO)_2BH_2^+$ ion, and Schaeffer, Tebbe and Phillips[12] only observed a very broad $(dioxane)_2BH_2^+$ signal. Apparently B^{11} quadrupole relaxation can be significant in ions of this type.[12] 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.

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. It might be more feasible to attempt conversion of $(H_2O)_2BH_2^+$ to an ether adduct, $(ether)_2BH_2^+$. It may be possible to precipitate 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 minutes, diborane was only half-reacted with 8 M HCl in three hours. 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 significantly reduce the rate.

Acknowledgments. - We wish to thank Drs. Malcolm Judkins and Robert Marianelli for obtaining the B^{11} nmr spectra. This research was supported by the United States Atomic Energy Commission.

References

(1) A preliminary report of these findings appears in W. L. Jolly and T. Schmitt, J. Am. Chem. Soc., __, (1966).

(2) W. L. Jolly and J. E. Drake, Inorg. Syntheses, 7, 34(1963).

(3) T. Schmitt, "Reactions of the Hydroborate Ion in Acidic Solutions," M.S. Thesis, University of California, Berkeley, Jan. 1966, University of California Radiation Laboratory Report UCRL-16659.

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

(5) R. T. Sanderson, "Vacuum Manipulation of Volatile Compounds," Wiley, New York, 1948.

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

(7) When diborane is allowed to react with ethanol-water solutions[1,6] at -75°, or with ice[8] at -80°, four moles of hydrogen are 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: $H_2OBH_2(OH) + H_2O \rightarrow H_2OBH(OH)_2 + H_2$. Apparently this latter hydrolysis is suppressed in the acidic solutions of the present investigation.

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

(9) 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.

(10) N. E. Miller and E. L. Muetterties, J. Am. Chem. Soc., 86, 1033 (1964).

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

(12) R. Schaeffer, F. Tebbe and C. Phillips, Inorg. Chem., 3, 1475(1964).

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

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