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Berkeley, California

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EVIDENCE FOR THE SPECIES BH_2^+ AND $\text{BH}(\text{OH})_2$ IN AQUEOUS SOLUTIONS.
THE REACTION OF DIBORANE WITH HYDROXIDE.

William L. Jolly and Theresa Schmitt

May 1966

Evidence for the Species BH_2^+ and $\text{BH}(\text{OH})_2$ in Aqueous Solutions.

The Reaction of Diborane with Hydroxide.

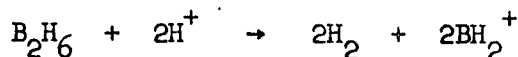
Sir:

We wish to report stoichiometric evidence for the formation of intermediates in the hydrolyses of diborane and hydroborate in aqueous solutions at temperatures around -70° . The data for strongly acidic solutions are consistent with the formation of the aquated BH_2^+ ion. The data for unacidified solutions of ethanol and water correspond to the formation of $\text{BH}(\text{OH})_2$ (or its hydrogen-bridged dimer), probably mixed with the various possible ethoxy derivatives. Studies with potassium hydroxide, in solution and in the solid state, suggest the formation of the $\text{BH}(\text{OH})_3^-$ ion.

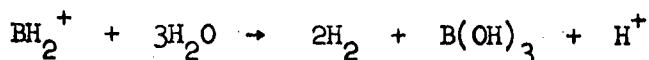
Evidence for BH_2^+ . - Potassium hydroborate reacts with 8 M HCl at -70° to form two moles of hydrogen per mole of hydroborate and a solution which is capable of reducing iodine and which yields another two moles of hydrogen when warmed above -20° .¹ Boron-11 n.m.r. spectra of cold solutions as concentrated as 2 N in the reducing species (determined both by iodine titration and hydrogen evolution) showed only an extremely broad peak² centered 29 ppm upfield from the signal of BCl_3 . After allowing such solutions to decompose at 0° , the broad peak disappeared, and a precipitate of boric acid formed.

Diborane reacts slowly⁶ with 8 M HCl at -75° to form always two moles of hydrogen per mole of diborane; four more moles of hydrogen are evolved upon warming the solution above -20°. The properties of the cold solution are identical to those of the solutions prepared by the addition of hydroborate to cold 8 M HCl. To determine whether chloride ion has a specific influence on the course of the reaction, the reaction of diborane with 5.4 M HClO₄ at -55° was studied. In two such experiments, 2.70 and 2.15 moles of hydrogen were slowly evolved per mole of diborane. We believe the principal reaction in these experiments was the same as that occurring in 8 M HCl at -75°, but that some extra hydrolysis occurred because the experiments were necessarily carried out at a considerably higher temperature and with a lower concentration of hydrogen ion.

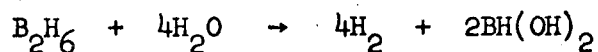
We believe that the reactions of hydroborate and diborane with cold aqueous acid may be expressed by the equations



and that the decomposition of the aquated BH_2^+ species above -20° may be written as follows.



Evidence for $\text{BH}(\text{OH})_2$. - When diborane reacts with ethanol-water solutions at temperatures around -75° , always four moles of hydrogen are evolved per mole of diborane. The resulting solution yields another two moles of hydrogen when warmed above -20° . These data suggest the formation and subsequent decomposition of $\text{BH}(\text{OH})_2$, $\text{BH}(\text{OH})(\text{OEt})$, and $\text{BH}(\text{OEt})_2$.⁷ Thus we might write, for the formation of $\text{BH}(\text{OH})_2$,



and for the decomposition of $\text{BH}(\text{OH})_2$,



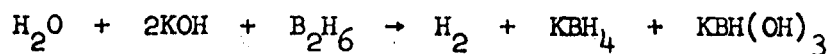
Of course, it is conceivable that hydrogen-bridged species such as $(\text{HO})_2\text{BH}_2\text{B}(\text{OH})_2$, $(\text{HO})_2\text{BH}_2\text{B}(\text{OH})(\text{OEt})$, etc., are formed, or that a cyclic compound such as boroxine ($\text{B}_3\text{O}_3\text{H}_3$) is formed, but in the absence of further data we prefer the above simple formulation.

When a solution prepared by the reaction of diborane with an ethanol-water solution at -75° is treated with an equal volume of 8 M HCl at the same temperature, no appreciable hydrogen is evolved. The resulting solution decomposes at approximately the same rate as solutions to which no acid has been added (at corresponding temperatures above -20°). These results suggest that the decomposition is not acid-catalyzed.

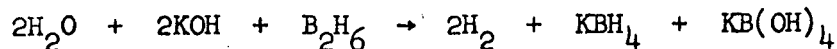
When a solution prepared by the reaction of diborane with an ethanol-water solution at -75° is treated with an ethanol-water solution of potassium hydroxide at the same temperature, only a small amount of

hydrogen is evolved. When the resulting solution is warmed to room temperature, approximately 1.3 moles of hydrogen per mole of diborane are rapidly evolved. A final 0.7 mole of hydrogen is very slowly evolved during a period of several days at room temperature, bringing the total evolved hydrogen to six moles per mole of diborane. We tentatively suggest that the addition of hydroxide to the cold solution caused the formation of a series of species such as $\text{BH}(\text{OH})_3^-$, $\text{BH}(\text{OH})_2(\text{OEt})^-$, etc., and that these species undergo hydrolysis upon warming the solution.¹⁰ Other experiments which may be interpreted as indicating the formation of $\text{BH}(\text{OH})_3^-$ are described below.

Reaction of B_2H_6 with KOH. - When diborane reacts at -30° with an excess of coarsely pulverized reagent grade KOH which has been allowed to absorb about 7% extra water, approximately 1.13 moles of hydrogen are evolved per mole of consumed diborane.¹⁴ When the resulting solid is dissolved in cold water, a small amount of hydrogen (about 0.15 moles per mole of consumed diborane) is rapidly evolved, and the resulting solution slowly evolves hydrogen for several days at room temperature.¹⁶ The latter observation is very significant in that it shows that, after the initial rapid evolution of hydrogen, the solution contains more reducing power than corresponds to the formation of equimolar amounts of borate and hydroborate. The stoichiometry may be explained by assuming that the principal over-all reaction of the diborane with potassium hydroxide is the following,



with the following side reaction occurring to some extent.



The latter reaction can be made essentially quantitative by allowing diborane to react with a concentrated KOH solution at -30° .^{14,17} All our attempts to obtain the boron-11 n.m.r. spectrum of the BH(OH)_3^- ion were unsuccessful; solutions of the B_2H_6 -solid KOH reaction product only yielded resonances attributable to B(OH)_4^- and BH_4^- . Possibly B^{11} nuclear quadrupole relaxation effects are responsible for our inability to see a signal. In this respect it is interesting to note that we were similarly unable to observe a proton nmr signal for the hydridic hydrogen of the aqueous trimethoxyhydroborate ion. Solutions prepared from NaBH(OMe)_3 showed, however, a signal corresponding to the hydroborate ion. The latter species may be attributable to impurity in the NaBH(OMe)_3 sample or to a disproportionation upon dissolution.²⁰

Acknowledgment. - We wish to thank Messrs. Malcolm Judkins and Robert Marianelli for obtaining the B^{11} n.m.r. spectra. This research was supported by the U.S. Atomic Energy Commission.

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References

- (1) Such data were obtained from experiments carried out in closed reaction vessels. However, when potassium hydroborate was added to 8 M HCl at -75° while rapidly pumping the evolved gas through a trap at -78° and a trap at -196° , a small amount (corresponding to a 2% yield) of diborane was collected in the -196° trap.
- (2) McAchran and Shore³ similarly were unable to observe a well-defined spectrum of the $\text{BH}_2(\text{OSMe}_2)_2^+$ ion, and Schaeffer, Tebbe and Phillips⁴ only observed a very broad $\text{BH}_2(\text{dioxane})_2^+$ signal. Apparently B^{11} quadrupole relaxation occurs in ions of the type $\text{BH}_2(\text{base})_2^+$.⁵
- (3) G. E. McAchran and S. G. Shore, Inorg. Chem., 4, 125(1965).
- (4) R. Schaeffer, F. Tebbe and C. Phillips, Inorg. Chem., 3, 1475(1964).
- (5) S. G. Shore, C. W. Hickam, Jr. and D. Cowles, J. Am. Chem. Soc., 87, 2755(1965).
- (6) Only about half of a 0.6 mmole sample of diborane reacted with 10 ml. of stirred 8 M HCl at -75° in a period of three hours.
- (7) Weiss and Shapiro⁸ found that 4 moles of hydrogen were evolved per mole of diborane consumed in the reaction with ice at -80° . They proposed the formation of -O-BH-O- groups attached to the surface of the ice. Lehmann, Weiss and Shapiro⁹ showed that $\text{BH}(\text{OEt})_2$ is a relatively stable material formed by the reaction of ethanol with excess diborane.
- (8) H. G. Weiss and I. Shapiro, J. Am. Chem. Soc., 75, 1221(1953).

- (9) W. J. Lehmann, H. G. Weiss and I. Shapiro, J. Chem. Phys., 30, 1222(1959).
- (10) Apparently only on the basis of the evolved hydrogen, Mikheeva and Surs¹¹ postulated the formation of $\text{BH}(\text{OH})_3^-$ as one of several intermediates in the reaction of B_2H_6 with KOH solutions. Mochalov and Gil'manshin¹² presented polarographic evidence for the same species, but Gardiner and Collat¹³ disputed their interpretation.
- (11) V. I. Mikheeva and V. Y. Surs, Dokl. Akad. Nauk S.S.S.R., 93, 67(1953); Chem. Abstr., 48, 7470c(1954).
- (12) K. N. Mochalov and G. G. Gil'manshin, Dokl. Akad. Nauk S.S.S.R., 132, 134(1960); Zh. Fiz. Khim., 36, 1089(1962).
- (13) J. A. Gardiner and J. W. Collat, Inorg. Chem., 4, 1208(1965).
- (14) These observations are in close agreement with those of Stock and Kuss,¹⁵ who observed that 1.1 moles of hydrogen per mole of diborane were evolved in the reaction of diborane with their driest sample of KOH. With increasing moisture content, the hydrogen evolution increased; 30% KOH solution yielded 2 moles of hydrogen per mole of diborane. Stock and Kuss explained their data in terms of the reaction $\text{B}_2\text{H}_6 + 2\text{KOH} \rightarrow 2\text{KOBH}_3 + \text{H}_2$.
- (15) A. Stock and E. Kuss, Chem. Ber., 47, 810(1914).
- (16) We cannot now account for the rapid initial evolution of hydrogen. Possibly this is attributable to a relatively unstable $\text{BH}_2(\text{OH})_2^-$ ion. The final rate of hydrogen evolution appears to be greater than that observed for KBH_4 in a solution of comparable alkalinity.

- (17) Davis and Gottbrath¹⁸ obtained 10-17% yield of hydroborate by bubbling diborane through NaOH solutions at 0°. Winternitz has alluded to the reaction, and has stated that he was unable to verify Stock's findings with regard to the reaction of diborane with potassium hydroxide.¹⁹
- (18) R. E. Davis and J. A. Gottbrath, Chem. and Ind., 1961, 1961.
- (19) P. F. Winternitz, in "Borax to Boranes," Advances in Chem. Series No. 32, A.C.S., Washington, D.C., 1961, p. 174.
- (20) H. C. Brown, E. J. Mead and P. A. Tierney, J. Am. Chem. Soc., 79, 5400(1957).

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