dipole-induced dipole. The latter two forces both result in an appreciable change in the electron distribution in the acid and are difficult to distinguish experimentally. As a result of contributions to the bonding from these two forces (3 and 4), the infrared stretching vibrations of the halogen molecules[10] undergo a pronounced decrease in frequency upon complexation. In contrast, the S-O stretching mode in the SO_2 adduct is not changed from that observed in SO_2. This evidence indicates that the interaction is essentially dipole–dipole in the SO_2 adduct.

There is general agreement that the electrostatic model does not provide an adequate description of the hydrogen bonding interaction. The inadequacies have been reviewed by Coulson.[11] As with the halogen acids, the O–H stretching vibration of phenol undergoes a marked decrease in frequency upon complexation. The heat of formation of the phenol adduct is much greater than that of the SO_2 adduct. Both of these observations are attributed to the fact that phenol is easily polarized and the phenol adduct has appreciable contributions from covalent and dipole-induced dipole interactions in addition to those of the dipole–dipole type. The enthalpies for this series of acids are interpreted qualitatively by considering the dipole moments and assigning the following order of decreasing polarizability and covalency toward DMA

$\mathrm{ICl} > \mathrm{I_2}$[12] $\gg \mathrm{C_6H_5OH} > \mathrm{Br_2} > \mathrm{SO_2}$

Since phenol and ICl have dipole moments close to that of SO_2 and since the former are much more polarizable, it is expected that SO_2 will be a weaker acid than phenol or ICl toward most donors.

Acknowledgment.—The authors would like to thank the Chemistry Branch of the Atomic Energy Commission for their generous support of this research through Contract No. AT(11-1) 758.

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[10] W. B. Person, R. E. Erickson and R. E. Buckles, *J. Am. Chem. Soc.*, **82**, 29 (1960), and papers referenced therein.

[11] C. A. Coulson, *Research* (London), **10**, 149–159 (1957), also (4) p. 233.

[12] The order for iodine and ICl cannot be distinguished with certainty but the very high heat of the ICl adduct (greater than the sum of I_2 plus SO_2) favors this sequence. The polarization of ICl surely increases its dipole moment in the adduct and results in greater dipole–dipole interaction.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND LAWRENCE RADIATION LABORATORY, UNIVERSITY OF CALIFORNIA, BERKELEY, CALIFORNIA]

The Exchange of Deuterium with Solid Potassium Hydroborate

BY ROBERT E. MESMER[1] AND WILLIAM L. JOLLY

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Potassium deuterioborate has been prepared by reaction of deuterium gas with potassium hydroborate at temperatures near 500°. It is proposed that both the exchange reaction and the pyrolysis proceed through the following initial dissociation: $BH_4^- \rightarrow H^- + {}^1/_2B_2H_6$. The proportions of the anions BH_4^-, BH_3D^-, $BH_2D_2^-$, BHD_3^- and BD_4^- in partially deuteriated samples have been deduced from the composition of the hydrogen evolved upon hydrolysis, from proton magnetic resonance spectra and from the magnitude of the equilibrium constant for exchange. The proportions of these anions in partially deuteriated samples which have been equilibrated at *ca.* 500° correspond to a random distribution of deuterium atoms.

Introduction

In order to study kinetic isotope effects of reactions of the hydroborate ion (BH_4^-), we needed an alkali metal deuterioborate (*e.g.*, KBD_4). Sodium deuterioborate has been prepared[2] from B_2D_6 and $NaB(OCH_3)_4$ and could probably be prepared[3] by the reaction of NaD with methyl borate. However, because it has been shown that tritium gas undergoes exchange with the hydrogen in lithium and sodium hydroborates at elevated temperatures,[4] we concluded that an analogous exchange reaction of deuterium gas might serve for the preparation of an alkali deuterioborate. Indeed, the latter method has been found very convenient for preparing potassium deuterioborate, and we present here the details of the synthesis.

Three pieces of evidence lead to the conclusion that, in partially deuteriated samples of potassium hydroborate which are at equilibrium, the relative amounts of the various anions (BH_4^-, BH_3D^-, etc.) are governed chiefly by statistics. These pieces of evidence (discussed below) involve: (1) the amounts of H_2, HD and D_2 evolved upon hydrolysis of samples in aqueous acid, (2) the proton magnetic resonance spectra of aqueous solutions of partially deuteriated samples and (3) the measured equilibrium constants for the solid–gas exchange reaction.

Discussion of Results

Preparation of Potassium Deuterioborate.—Initially, attempts were made to carry out the exchange reaction by heating potassium hydroborate at 430° in 1/3 atm. of deuterium gas. Working with such a low pressure of hydrogen was unsatisfactory not only because of the necessity of handling large volumes of gas, but also because most of the sample decomposed to a dark solid and a mixture of boron hydrides. When deuterium gas pressures of 70–100 atm. were used, it was possible to work at temperatures as high as 538° with only slight decomposition in a three-day period. These results are in agreement with the findings of Ostroff

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[1] Taken from a thesis presented by R. E. Mesmer for partial satisfaction of the requirements of the Ph.D. degree, University of California, Berkeley, 1962.

[2] R. E. Davis, C. L. Kibby and C. G. Swain, *J. Am. Chem. Soc.*, **82**, 5950 (1960).

[3] H. C. Brown, E. J. Mead and P. A. Tierney, *ibid.*, **79**, 5400 (1957).

[4] W. G. Brown, L. Kaplan and K. E. Wilzbach, *ibid.*, **74**, 1343 (1952).

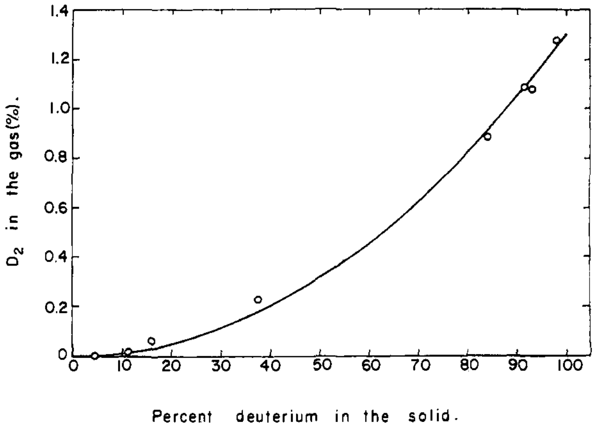

Fig. 1.—Plot of the percentage D_2 in the gas evolved in the complete hydrolysis of partially deuterated hydroborate samples *versus* the percentage D in the samples.

and Sanderson,[5] who observed that decomposition of sodium and potassium hydroborates began at a higher temperature in hydrogen than in nitrogen. It seems likely that an early step in the decomposition involves the reversible evolution of molecular hydrogen. Although Schlesinger and Brown[6] report the reversible evolution of essentially pure hydrogen gas from lithium hydroborate, we suggest that, in the case of sodium and potassium hydroborates, the initial reaction involves the reversible evolution of diborane. As supporting evidence for diborane evolution, we have our observations for the potassium salt and a literature report[7] for the sodium salt. We propose that, at a sufficiently high pressure of hydrogen (or deuterium), the following equilibrium is established

$$KBH_4 = KH + {}^1/_2B_2H_6 \qquad (1)$$

(We do not suggest that a separate KH phase forms, but rather that hydride ions replace hydroborate ions in the KBH_4 lattice.) Under these conditions, the equilibrium pressure of diborane is a function of temperature alone. Since exchange between deuterium gas and diborane is rapid at the temperatures studied,[8] a mechanism is available for the exchange of deuterium with the hydroborate. When the hydrogen pressure is below the equilibrium dissociation pressure of the alkali metal hydride, the equilibrium established is

$$KBH_4 = K + {}^1/_2H_2 + {}^1/_2B_2H_6 \qquad (2)$$

Then the lower the pressure of hydrogen, the higher will be the equilibrium pressure of diborane. Presumably, when the pressure of hydrogen is low enough, the pressure of diborane increases to the point where its irreversible pyrolysis (1.5 order in $P_{B_2H_6}$)[9] becomes important.

Hydrolysis of Partially Deuterated Hydroborate.—We determined the percentages of deuterium in the samples of partially deuterated hydroborate by mass-spectrometric analysis of the hydrogen formed in the complete hydrolyses of the samples in acidic light water. It was assumed that one half of the evolved hydrogen originated from the hydroborate and that the other half originated from the water. Thus the percentage of deuterium in a hydroborate sample was calculated as the percentage of HD in the hydrogen plus two times the percentage of D_2 in the hydrogen. Some justification for this procedure may be found in the facts that (a) roughly equal amounts of H_2 and D_2 were formed in the hydrolysis of BH_4^- in high-purity heavy water, (b) the ratio of H_2 to D_2 formed in hydrolyses of deuterioborate in ordinary water approached unity as the deuterium content of the deuterioborate approached 100%, and (c) the amount of "odd" hydrogen (D_2 in the case of hydrolyses in ordinary water and H_2 in the case of hydrolyses in D_2O) was usually only 3–5% of the amount of HD.

In Fig. 1 we have plotted the percentage of D_2 in the hydrogen from the complete hydrolysis (in H_2O) of hydroborate samples as a function of the percentage deuterium in the samples. The curve was constructed on the basis of certain assumptions which follow. Evidence to be presented elsewhere[10] indicates that an intermediate of composition BH_5 forms in the hydrolysis of hydroborate. Consider the intermediate BD_4H which forms in the hydrolysis of BD_4^- in H_2O. Most of this intermediate breaks up by a non-random process to give HD and BD_3, but a small portion breaks up by an apparently random process to give HD and D_2 in a ratio of 2 to 3. Presumably these break-ups can proceed stepwise through intermediates such as $BD_3(OH)H$, etc., until the sample is completely converted to boric acid or borate. By assuming that partially deuteriated hydroborate samples contain statistical amounts of species such as BD_4^-, BD_3H^-, etc., and by assuming that each species hydrolyzes by a mechanism similar to that described above, we can calculate for Fig. 1 a family of curves, each corresponding to a different ratio of random to non-random breakups. The curve plotted in Fig. 1 corresponds to break-ups which are 5.2% random. The fact that the experimental points fit the theoretical curve indicates that our assumption regarding the statistical population of BD_4^-, BD_3H^-, etc., is reasonable. One example of a non-statistical distribution is the situation where the only species are BH_4^- and BD_4^-. Under such circumstances, the curve would be a straight line.

Proton Magnetic Resonance Studies.—The proton magnetic resonance spectra were obtained for aqueous solutions of partially deuteriated hydroborate samples which had been allowed to reach equilibrium with deuterium–hydrogen mixtures at 500°. A sample containing 37.4% deuterium gave a spectrum (Fig. 2) which can be resolved into three component spectra that are attributable to BH_4^-, BH_3D^- and $BH_2D_2^-$. The relative areas of these component spectra (after multiplying the BH_3D^- area by 4/3 and the $BH_2D_2^-$ area by 2) are 1:2.4:2.0. These ratios are almost the same as those one would expect for a completely random distribution of hydrogen and deuterium, namely 1:2.31:2.14.

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(5) A. G. Ostroff and R. T. Sanderson, *J. Inorg. Nuclear Chem.*, **4**, 230 (1957).

(6) H. I. Schlesinger and H. C. Brown, *J. Am. Chem. Soc.*, **62**, 3429 (1940).

(7) Metal Hydrides, Inc., Technical Bulletin 502, "Sodium Borohydride."

(8) F. J. Norton, *Science*, **111**, 202 (1950).

(9) J. K. Bragg, L. V. McCarty and F. J. Norton, *J. Am. Chem. Soc.*, **73**, 2134 (1951).

(10) Unpublished observations of R. Mesmer and W. Jolly.

The proton signal of hydroborate is shifted to a higher field when one, two or three of the hydrogen atoms are replaced by deuterium atoms. This chemical shift is in agreement with the general observation that deuterium is more electron-releasing than hydrogen.[11] It is interesting to note that the chemical shift is directly proportional to the number of deuterium atoms, amounting to 0.020 p.p.m. per deuterium atom. The spectra also give the coupling constants for the proton-proton interaction on the hydroborate ion. This coupling constant is 10.7 ± 0.3 c.p.s. and may be compared with the corresponding coupling constant in methane[12] of 12.4. This trend is consistent with the bond lengths in BH_4^- and CH_4 of 1.26 and 1.09 Å., respectively.

Equilibrium Measurements.—The reaction of deuterium with hydroborate may be represented by the equation

$$B\text{-}H + D_2 = B\text{-}D + HD \qquad (3)$$

At equilibrium, the following equilibrium expression should hold

$$K = \frac{(HD)}{(D_2)} \cdot \frac{(B\text{-}D)}{(B\text{-}H)}$$

where (B–D)/(B–H) is the ratio of deuterium to hydrogen in the solid. The following facts support the conclusion that equilibrium was achieved in the reactions between deuterium and potassium hydroborate at 538°: (1) Sufficient time was allowed for the isotopic composition of the hydrogen over the solid to become constant. The quotient $(HD)^2/(H_2)(D_2)$, calculated from the composition of the hydrogen, generally ranged between 3.67 and 3.95, as compared with the theoretical constant of 3.81 for the following reaction.[13]

$$H_2 + D_2 = 2HD \qquad (4)$$

(2) The same value was obtained for the equilibrium constant of equation 3 when equilibrium was approached from either direction, that is, when deuterium was introduced as the gas or as the hydroborate. (3) The same value was obtained for the equilibrium constant for widely differing overall deuterium concentrations. The observed equilibrium constants for equation 3 are tabulated in Table I. The average value, 2.05 ± 0.03, is close to the value 2.00, which one would expect if the hydrogen isotopes were randomly distributed in the solid and the gas.[14] Thus, if we assume that partially deuteriated samples contain the various ions BH_4^-, BH_3D^-, $BH_2D_2^-$, BHD_3^- and BD_4^-, it is clear that the proportions of these ions in a given sample are determined by statistics.

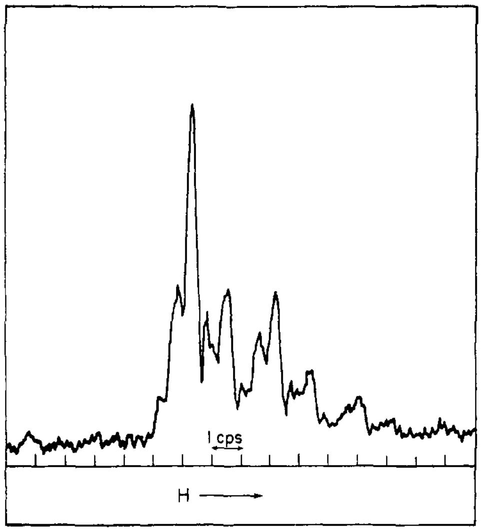

Fig. 2.—Proton magnetic resonance spectrum of an aqueous solution of partially deuteriated potassium hydroborate (37.4% D).

The data of Brown, *et al.*,[3] for the exchange of tritum with lithium and sodium hydroborates may be used to calculate values for the quotient $(H_2)/(HT) \cdot (B\text{-}T)/(B\text{-}H)$, for which the statistical value is 0.50. For $LiBH_4$ at 200° quotients approximating this value (0.55, 0.47 and 0.68) were obtained only in runs of long duration. For $NaBH_4$, equilibrium was probably never attained, but the closest approach to equilibrium (quotient 0.22) was attained in their highest-temperature run (375°). It is apparent that the rate of exchange of molecular hydrogen with alkali metal hydroborates decreases at a given temperature on going from lithium to potassium.

TABLE I

OBSERVED EQUILIBRIUM CONSTANTS FOR EQUATION 3 AT 538°

$(HD)/(D_2)$	$K = \frac{(HD)}{(D_2)} \cdot \frac{(B\text{-}D)}{(B\text{-}H)}$
0.151	1.99
0.387	2.06
16.4	2.09
42.4	2.06

Experimental

Preparation of Potassium Deuterioborate.—After heating a 0.25 g. sample of KBH_4 in 25 cm. of D_2 for 30 hr. at 430°, there was appreciable decomposition of the hydroborate to give a dark reddish-brown deposit on the cool part of the tube. The crude solid product was gray and a strong odor of boron hydrides was noted while removing the solid. The D_2 was removed and replenished three times during this run. Forty-five per cent of the hydroborate was recovered and 16% was converted to deuterioborate.

The apparatus used in the high pressure deuteriation consisted of a 70-cc. hydrogenation bomb fitted with steel pressure tubing, a pressure gage and needle valves. A cylinder of 99.4% deuterium gas from General Dynamics Corp. was used in all preparations of deuterioborate. The bomb was heated by means of a large tube furnace and the temperature recorded with a Chromel-Alumel thermocouple.

The products were purified by extraction with anhydrous liquid ammonia in a sealed vessel containing a glass wool filter.

One g. of KBH_4 treated at 500° for 72 hr. with 50 atm. of D_2 (measured at room temperature) gave an 84% yield of purified product. An X-ray powder pattern on the material which was insoluble in liquid ammonia indicated the presence of KBO_2 and KOH. The purified product contained 98.8% deuterium as determined by the acid hydrolysis method.

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[11] L. Melander, "Isotope Effects on Reaction Rates," Ronald Press Co., New York, N. Y., 1960, pp. 89–93.

[12] M. Karplus, D. H. Anderson, T. C. Farrar and H. S. Gutowsky, *J. Chem. Phys.*, **27**, 597 (1957).

[13] This result is a necessary, but insufficient, condition for equilibrium. In run 1 (see Experimental) the equilibrium quotient for equation 4 became constant long before the isotopic composition of the hydrogen did. It appears, therefore, that equilibration in reaction 4 is more rapid than the equilibration of deuterium and hydrogen with the solid.

[14] Similarly the average value of 0.54 for $(H_2)/(HD) \cdot (B\text{-}D)/(B\text{-}H)$ is close to the statistical value 0.50.

Hydrolysis of Partially Deuteriated Hydroborate.—The percentages of deuterium and hydrogen in the solid hydroborates were determined by mass analysis of the gases evolved from 6 *N* sulfuric acid solution. The mass analyses were performed on the Type 21-103 A Consolidated Engineering Corp. Mass Spectrometer III at the Lawrence Radiation Laboratory. The detailed description of the method used in determining H_2, HD and D_2 composition has been described by Newton and Mohler.[15] The results are given graphically in Fig. 1.

Proton Magnetic Resonance Studies.—The proton magnetic resonance spectra of aqueous solutions of partially deuteriated hydroborate were recorded on a Varian A-60 spectrometer. The proton spectrum, as was previously reported by Ogg,[16] consists of four lines due to interaction with the B^{11} ($I = 3/2$) and seven lines due to B^{10} ($I = 3$). The relative abundances of these boron isotopes are 81.17 and 18.83 %, respectively. The spectrum taken with a 50 c.p.s. sweep width is shown in Fig. 2. This spectrum represents one of the four equivalent lines due to B^{11} in a solution of 1.0 M hydroxide and 0.85 *M* hydroborate (37.4% D).

The spectrum is readily interpreted if one considers the spectra expected for BH_3D^-, $BH_2D_2^-$ and BHD_3^-. Each of the lines due to coupling of the proton spins with B^{11} spins is slit by the deuterium nuclei present. In the case of BH_3D^-, each line is split into a triplet with equal intensities: in $BH_2D_2^-$ each is split into a quintet with intensities 1:2:3:2:1, and in BHD_3^- each is split into a septet with intensities 1:3:6:7:6:3:1.

For the assignment of the spectrum the statistical composition of the solid is helpful. A sample containing 37.4% deuterium distributed randomly in the solid has the composition: 15.4% BH_4^-, 36.7% BH_3D^-, 32.9% $BH_2D_2^-$, 13.1% BHD_3^- and 2.0% BD_4^-. Of course, there is no proton spectrum due to BD_4^- and the spectrum due to BD_3H^- would not be detected in this mixture. The most intense line in the spectrum is assigned to BH_4^-. Next in intensity are the 3 lines of BH_3D^- of which two are on the right and one on the left of the BH_4^- line. The smaller lines are attributable to $BH_2D_2^-$. With this assignment of lines we measure ratios of 1:2.4 ± 0.3:2.0 ± 0.4 for BH_4^-:BH_3D^-:$BH_2D_2^-$.

A spectrum of a sample containing 84.2% D consisted of a broad peak whose center was shifted slightly to the right from the spectrum of the 37.4%D sample. The signal-to-noise ratio was too low for resolution of the lines present.

The coupling constant in BH_3D^- due to deuterium-hydrogen coupling is 1.65 ± 0.05 c.p.s.; in $BH_2D_2^-$ the same constant is 1.7 ± 0.1 c.p.s. From these data one calculates[17] a hydrogen–hydrogen coupling constant for hydroborate of 10.7 ± 0.3 c.p.s.

Equilibrium Measurements.—The apparatus used in the preparation of potassium deuterioborate was used to measure quantitatively the distribution of deuterium between the solid and gas at 538 ± 2°. A tank of deuterium gas (99.37%) and a 1000-psi pressure gage were attached by heavy-walled steel pressure tubing. Needle valves were also inserted for removal of samples and for handling the apparatus during the cooling procedure.

Before adding D_2 the system was evacuated. In two of the runs the D_2 cyclinder was replaced by an H_2 cylinder and the deuterium was introduced as partially deuteriated hydroborate. Samples of gas were taken by bleeding a small sample into a section of tubing between two needle valves. Traces of diborane were always present in these gas samples.

The apparatus was cooled suddenly by removing the bomb from the furnace and immediately placing it in front of a powerful electric fan. Experiments showed that the temperature diminished about 100° in the first 3 min., and 200° in the first 8 min. when commencing at 538°. Table II lists the compositions of the gas phase for various times and of the gas evolved from the hydrolysis of the solid when the experiment was terminated. The half-life of this approach to equilibrium is 5 to 7 hr. at 538°. This indicates that our cooling rate was sufficient to quench the equilibrium at 538°.

TABLE II

EXPERIMENTAL DATA FOR EQUILIBRIUM AT 811°K.

Run 1. Analyses of gas at various times (%)

Time (hr.):	0	12	34	Cooled after 34 hr.	Analysis of solid (%)
H_2	0	2.19	2.80	2.95	16.71
HD	1.25	24.31	27.42	27.07	82.40
D_2	98.75	73.50	69.77	69.95	0.89
D	99.37	85.65	83.48	83.48	
K^a	∞	3.67	3.85	3.55	

Run 2. Analysis of gas (%)

Time:	Cooled after 62 hr.	Analysis of solid (%)
H_2	0.48	8.15
HD	13.06	90.77
D_2	86.46	1.08
D	93.99	
K^a	4.10	

Run 3. Analysis of gas (%)

Time:	Cooled after 68 hr.	Analysis of solid (%)
H_2	79.86	88.69
HD	18.98	11.29
D_2	1.16	0.02
D	10.65	
K^a	3.89	

Run 4. Analyses of gas at various times (%)

Time: (hr.)	12	42	65	Cooled after 65 hr.	Analysis of solid (%)
H_2	93.85	91.07	91.55	91.31	95.38
HD	6.05	8.71	8.25	8.49	4.62
D_2	0.10	0.22	0.20	0.20	0.00
D	3.12	4.58	4.33	4.45	
K^a	3.90	3.79	3.72	3.95	

[a] Equilibrium constant for reaction 4.

Acknowledgments.—We wish to thank Dr. Amos Newton and Mr. Aldo Sciamanna for the mass-spectrometric data. This research was supported by the U. S. Atomic Energy Commission.

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[17] J. A. Pople, W. G. Schneider and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw–Hill Book Co., New York, N. Y., 1959, p. 188.