Solvent Isotope Effects on Tetrahydridoborate Hydrolysis[1a]

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Abstract: Part of the product of the first step of the acid-catalyzed hydrolysis of BH_4^- has been trapped as BH_3CN^-, which is stable at the pH used. This permits the evaluation of the isotopic composition of the H_2 produced in the first step of the four-step hydrolysis. The isotopic composition of the product of the first step was then compared with that of the solvent from which it was made. The isotope effect, $(\kappa_H/\kappa_D)_H$, is between 2.2 and 1.4. When the excess of H over D in the hydronium ion formed in an isotopically mixed solvent is taken into account, this leads to a primary isotope effect, $(k_H/k_D)_I$, of not more than 1.5. Since the overall kinetic solvent isotope effect is at least 1.5, the secondary solvent isotope effect, $(k_H/k_D)_{II}$, appears, unprecedentedly, to be equal to or greater than 1.0. This, and other experimental evidence, is reconcilable if the last step of the diffusion process, in which H_3O^+ comes into direct contact with BH_4^-, is considered to be rate determining.

The object of this work was to separate the primary hydrogen isotope effect in the first step of the aqueous solution hydrolysis of tetrahydridoborate (eq 1)[2]

$$BH_4^- + H^+ \longrightarrow (H_2BH_3) \longrightarrow BH_3 + H_2 \qquad (1)$$

$$BH_3 \xrightarrow{H^+} \xrightarrow[\text{fast}]{H_2O} 3H_2 + B(OH)_4^- \qquad (2)$$

from the isotope effect on succeeding steps (eq 2) in the hope of relating the information obtained to the mechanism of the reaction. To do this, cyanide ion, known to be a strong nucleophile, was used to trap part of the BH_3 (eq 3). Trihydridocyanoborate is known to be stable under the reaction conditions.[3]

$$BH_3 + CN^- \longrightarrow BH_3CN^- \qquad (3)$$

Experimental Section

Product Composition. The NaCN solutions were allowed to react for 37 days in 0.01 *M* aqueous NaOH giving ~96% consumption of BH_4^-. Iodometric titrations[4,5] were then used to determine (1) the total reducing power of BH_3CN^- and BH_4^- in the solutions and (2) the reducing power of just the BH_3CN^- after the BH_4^- was completely hydrolyzed with an equal quantity of glacial acetic acid. The ratio of the rate constant for the reactions of BH_3 or its hydrate with water (k_{H_2O}) to that for reaction with CN^-(k_{CN}) was calculated assuming unit activity for water and CN^- activity equal to its concentration. It is given by eq 4. Borate concentration, ($B(OH)_4^-$),

$$k_{CN}/k_{H_2O} = (BH_3CN^-)/(\text{borate})(CN^-) \qquad (4)$$

is equal to the initial BH_4^- concentration minus both the BH_4^- concentration remaining and the cyanoborohydride formed. The fraction of untrapped material is *f* and is given by eq 5.

$$f = (\text{borate})/[(\text{borate}) + (BH_3CN^-)] \qquad (5)$$

$$1/f = 1 + (k_{CN}/k_{H_2O})(CN^-) \qquad (6)$$

Iodometric Titrations. The iodometric titration[4,5] was modified in order to handle smaller and more dilute solutions of hydridoborates. Hydridoborate solution (3 ml) was added to 20 ml of standard KIO_3 (about 0.25 *N*) which had been basified with two NaOH pellets (about 0.4 g) making the solution about 0.5 *M* NaOH. KI (1 g) was added and dissolved, followed by the addition of 10 ml of 4 *N* H_2SO_4. The solution was left in the dark for about 2 min and was then titrated with standard sodium thiosulfate (about 0.1 *N*) using amylose starch as indicator.

Gas Collection and Analysis. Hydrogen gas of unknown isotopic composition was obtained in the following manner. About 0.004 mol of $NaBH_4$ was made up in 50 ml of 6.85% D_2O,[6] 0.0113 *M* in NaOH. The flask was evacuated and allowed to stand in a constant temperature bath until about 0.01 mol of gas had formed (in 3.5 weeks about 88% reaction occurs). Another solution of 0.004 mol of $NaBH_4$ and 3 *M* NaCN were similarly made up and allowed to react. The gas from each sample was collected through a drying tube and analyzed for the ratio of H_2 to HD on a Nier 60° magnetic sector isotope ratio mass spectrometer.[7] The machine was calibrated with two standards which bracketed the unknowns. One was a sample assumed to have natural isotopic abundance,[8] and the second standard was analyzed commercially[9] by comparison with Bureau of Standards samples.

Results

Trapping of BH_3. Table I gives the fraction, *f*, of untrapped material in the various reaction mixtures. If $f = 0$, there is complete trapping, and if $f = 1$, there is no trapping. Table I also shows the derived ratio, k_{CN}/k_{H_2O}, which should be constant. Its average value is 0.091.

Table I. Fraction Untrapped in Various Concentrations of NaOH and NaCN

NaOH, *M*	NaCN, *M*	k_{CN}/k_{H_2O}	*f*
0.0113	1	0.089	0.918
0.0113	2	0.088	0.850
0.0113	3	0.095	0.778

Identification of BH_3CN^-. The nmr spectrum obtained from a partially hydrolyzed solution of BH_4^- in basic D_2O containing 3 *M* CN^- is shown in Figure 1. In addition to residual H_2O it revealed two quartets and a septet. The largest quartet is due to the residual $^{11}BH_4^-$ in the solution, and the septet is due to the $^{10}BH_4^-$. The smaller quartet is the BH_3CN^- pattern.[3] The septet corresponding to the BH_3CN^- is too weak to be seen in this spectrum. This gives a qualitative

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[1] (a) Supported, in part, by the National Science Foundation through GP-13172; (b) National Science Foundation Summer Research Participant, 1969.

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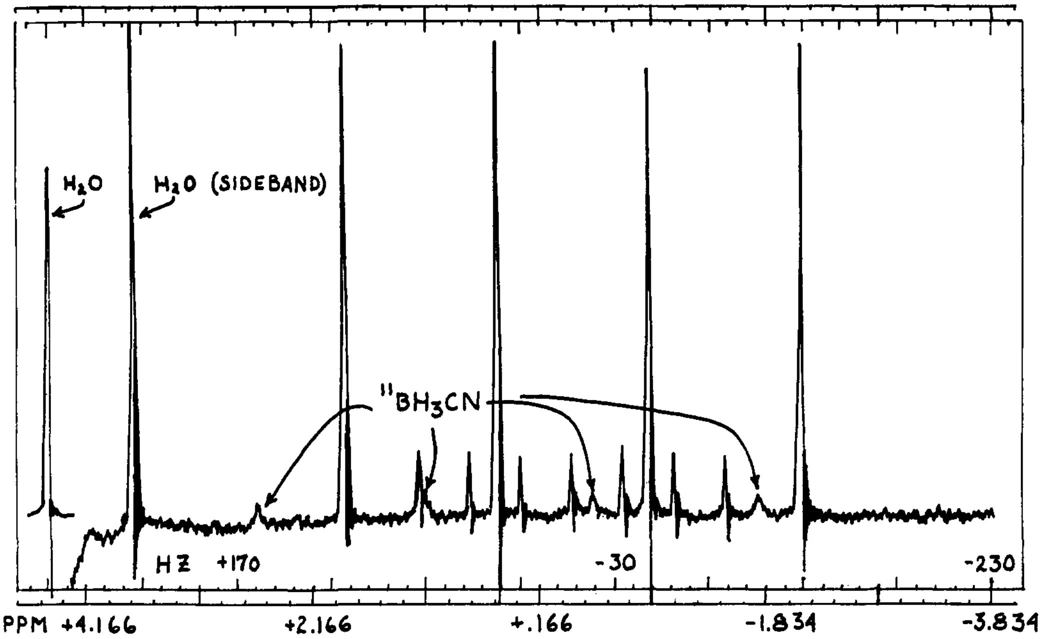

Figure 1. 60 MHz proton nmr spectrum of M BH_4^- partially hydrolyzed in basic D_2O containing 3 M CN^-. The chemical shifts are measured from the tetramethylsilane peak, although that peak is not shown on this spectrum. The main H_2O peak is much attenuated by comparison with the rest of the spectrum.

but firm indication that the cyanide ion traps BH_3 or its hydrate and forms BH_3CN^-.

Isotope Ratios. The H_2/HD ratio produced by various reaction mixtures is given in Table II. The differences between the ratios produced in the presence and absence of CN^- are small but statistically significant. The two distributions are different with a level of confidence[10] greater than 99.5%. Since trapping changes the relative amounts of H_2 produced in the first and subsequent steps, the isotopic ratio in the product of the first step, $(H_2/HD)_1$, should be calculated from eq 7.

$$\left(\frac{H_2}{HD}\right)_1 = \frac{3fM^i - fM^iM^u - 4fM^u + M^iM^u + M^i}{3fM^u - 4fM^i - f + M^u + 1} \qquad (7)$$

Here, f is defined by eq 5. The superscripts u and i indicate the absence or presence of 3 M NaCN, respectively. This equation was obtained by straightforward algebra from eq 8 to 13. The subscripts 1 and 2 refer to the liberation of gas from reactions shown

$$\{(H_2)_1{}^u + (HD)_1{}^u\} = 1/3\{(H_2)_2{}^u + (HD)^u\} \qquad (8)$$

$$\{(H_2)_1{}^i + (HD)_1{}^i\} = 1/(3f)\{(H_2)_2{}^i + (HD)_2{}^i\} \qquad (9)$$

$$(H_2/HD)_1{}^u = (H_2/HD)_1{}^i \equiv (H_2/HD)_1 \qquad (10)$$

$$(H_2/HD)_2{}^u = (H_2/HD)_2{}^i \equiv (H_2/HD)_2 \qquad (11)$$

$$M^i = \{(H_2)_1{}^i + (H_2)_2{}^i\}/\{(HD)_1{}^i + (HD_2)^i\} \qquad (12)$$

$$M^u = \{(H_2)_1{}^u + (H_2)_2{}^u\}/\{(HD)_1{}^u + (HD)_2{}^u\} \qquad (13)$$

in eq 1 and 2. M^i and M^u are 19.32 ± 0.03 and 19.10 ± 0.03, respectively. The value of f used in the calculation of $(H_2/HD)_1$ was obtained for 3 M CN^- from eq 6 and the average value of k_{CN}/k_{H_2O}. It is 0.78, and $(H_2/HD)_1$ is 23.2 ± 0.2. This value is not very sensitive to f because M^u and M^i are quite similar. The cited uncertainties are probable errors and were obtained from the scatter on replication of the primary, measured quantities by the usual techniques for propagation of errors.[11]

Table II. Isotopic Product Ratios in 6.85% D_2O

NaCN, M	HD/H_2[a]	M
0	0.0521	19.19
0	0.0526	19.01
0	0.0526	19.01
0	0.0521	19.19
0	0.0525	19.05
0	0.0523	19.12
0	0.519	19.27
3	0.0516	19.38
3	0.0516	19.38
3	C.0516	19.38
3	0.0520	19.23
3	0.0520	19.23

M^u = 19.10 ± 0.03 ((NaCN) = 0)
M^i = 19.32 ± 0.03 ((NaCN) = 3)

[a] Isotope ratio machine reading, the probable error determined by replication, is 0.0005.

Discussion

The foregoing results lead to a value of 1.7 ± 0.1 for κ_H/κ_D[12] for the first step and an average value of 1.3 ± 0.1 for the second and subsequent steps of the borohydride hydrolysis reaction. (The average isotopic composition of the transferring proton in the transition state is compared with the isotopic composition of the solvent by κ_H/κ_D.) Both values of κ_H/κ_D are averages of the value appropriate to the H^+-catalyzed reaction, $(\kappa_H/\kappa_D)_H$, and that for the reaction with water, $(\kappa_H/\kappa_D)_{H_2O}$. At this H^+ concentration (the pH was about 12) about 80% of the first step of the reaction is due to

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proton transfer from H^+ and about 20% to proton transfer from H_2O.[13] In practice, however, $(\kappa_H/\kappa_D)_H$ must be close to (κ_H/κ_D). If $(\kappa_H/\kappa_D)_{H_2O}$ is less than $(\kappa_H/\kappa_D)_H$, it is *most* unlikely to be less than 1.0. If it has the latter value, and the H_2O-promoted reaction is 20% of the whole, then $(\kappa_H/\kappa_D)_H$ is 2.0 instead of 1.7. If $(\kappa_H/\kappa_D)_{H_2O}$ is larger than 1.7, which is likely, then $(\kappa_H/\kappa_D)_H$ is smaller, but in any event, it is unlikely to be smaller than 1.4. Considering both the experimental uncertainties and those introduced by the water-promoted reaction, 2.2 and 1.4 seem like conservative outer limits for $(\delta_H/\kappa_D)_H$. Even the higher of these is substantially below the lowest previously reported values of $(\kappa_H/\kappa_D)_H$ which are around 4.[14] However, such a value can be rationalized by considering the rest of the experimental evidence.

The substitution of deuterium for hydrogen in an aqueous solvent leads to two isotope effects which can usually be found by considering the solvent isotope effect and the isotopic composition of the product of the reaction. The primary isotope effect, $(k_H/k_D)_I$, arises from the hydrogen or deuterium being transferred in the reaction while the secondary effect, $(k_H/k_D)_{II}$, is due to changes in frequencies at the nonreacting bonds. The primary effect can be determined in the following manner. In all of the following, M can be either H or D but must be the same on both sides of the equation. The equilibrium constant, *l*, for the reaction shown in eq 14 has been found equal to 0.69

$$D_{(M_2O)} + H_{(M_3O^+)} \overset{l}{\rightleftarrows} H_{(M_2O)} + D_{(M_3O^+)} \qquad (14)$$

± 0.02.[12,15–17] Equations 15 and 16 express the competition of the transition state, $\ddagger$, for the deuterium or hydrogen in the hydronium ion and hence the primary effect, $(k_H/k_D)_I$, is the ratio of the rate constants for these two reactions. Since $\ddagger_{HH}$ leads to H_2 and $\ddagger_{HD}$ leads to HD, the two transition states must be formed in the same ratio as the two products, and that ratio is given by $(\kappa_H/\kappa_D)_H \times (D/H)_{solv}$.[12] The value obtained refers to the transferring proton only, but the effective starting environment of that proton is that of the bulk solvent rather than the M_3O^+ unit as in eq 15 and 16.

$$M_2{}^+OH + BH_4{}^- \rightleftarrows \ddagger_{HH} + M_2O \qquad (15)$$

$$M_2{}^+OD + BH_4{}^- \rightleftarrows \ddagger_{HD} + M_2O \qquad (16)$$

Thus $(\kappa_H/\kappa_D)_H$ is the ratio of the equilibrium constants for the reactions shown in eq 17 and 18, and $(k_H/k_D)_I$

$$H_{(solv)} + BH_4{}^- \rightleftarrows \ddagger_{HH} \qquad (17)$$

$$D_{(solv)} + BH_4{}^- \rightleftarrows \ddagger_{HD} \qquad (18)$$

$$(\kappa_H/\kappa_D)_H = (H_2/HD)(D/H)_{solv} \qquad (19)$$

can be obtained by combining eq 14 and 19, with the result shown in eq 20. (This treatment neglects "medium isotope effects" as has been done in the evaluation of l[15–17] and in the reactions with which comparison is made.[12,20]) Using the limits on $(\kappa_H/\kappa_D)_H$ deduced above $1.5 > (k_H/k_D)_I > 0.9$.

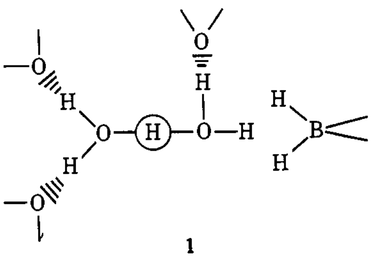
$$(k_H/k_D)_I = (k_H/k_D)_H \times l \qquad (20)$$

The secondary hydrogen isotope effect is given by eq 21[12] where k_H/k_D is the overall solvent isotope effect,

$$k_H/k_D = (k_H/k_D)_I(k_H/k_D)_{II} \qquad (21)$$

the rate ratio obtained for the reaction in H_2O and D_2O, respectively. Values of 1.9,[13] 1.6,[18] and 1.3[19] have been reported for k_H/k_D. The first, which we believe to be the best, has a probable error of 0.2 and the second appears to have a probable error of around 0.3.[13] The third of these, which is the only one which would jeopardize the conclusions reached below, is reported only as a footnote, in correction of earlier, quite different values, with no quantitative indication of its reliability. It seems quite safe, therefore, to limit k_H/k_D to values between 2.0 and 1.5. The lower limit for $(k_H/k_D)_{II}$, obtained by combining the lowest allowed value of k_H/k_D with the highest allowed value of $(k_H/k_D)_I$, is 1.0. More probable values are higher, around 1.5. Such values of $(k_H/k_D)_{II}$ have not been previously reported[12,20] but will be shown consistent with the other features of this reaction.

If the rate-determining step in the H^+-catalyzed $BH_4{}^-$ hydrolysis were diffusion controlled, much of the foregoing would be understandable. The solvent isotope effect on the diffusion controlled recombination of H^+ and OH^- is 1.7,[21] and diffusion of H^+ in aqueous HCl is faster than that of D^+ in D_2O–DCl by a factor of 1.4.[22] In such a mechanism the actual proton transfer to $BH_4{}^-$ would have to be very fast and might reasonably have a very small isotope effect. Since the isotopic composition of the product would be determined in a step subsequent to the rate-determining step, the separation of k_H/k_D into primary and secondary components, in eq 21, would have only formal significance. An apparently insurmountable obstacle to this explanation, however, is the value of k_H, 10^6 l. mol^{-1} sec^{-1},[13] fully four powers of ten below the values usually expected of diffusion controlled reactions. To overcome this problem it is postulated that the last step in the proton transport process is rate determining, that is, the step in which the H_3O^+ unit is brought in direct contact with $BH_4{}^-$. The postulated transition state is **1**. This resembles a proton diffusion step in most respects except that its standard free energy and activation free energy are higher because of the resultant



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interpenetration of hydration shells. This interpenetration results in the loss of one of the strong hydrogen bonds of the H_9O_4 unit.[23] This transition state is also consistent with the observation of a small, inverse, isotope effect, between 0.67 and 0.77, when BD_4^- is substituted for BH_4^-,[24] because the binding of the BH_4^- anion to its neighbors in solution is being strengthened, while no B–H bond is being broken. Hammes[25] has found a mechanism related to this in which the rate-determining step of the dimerization of 2-pyridone in DMSO mixtures is the dissociation of the dimethyl sulfoxide–2-pyridone hydrogen bond.

It is interesting to note that the magnitude of k_H (10^6 M^{-1} sec^{-1})[13] leads to a free energy of activation of 9.3 kcal mol^{-1}. The standard free energy of bringing together the reagents for an acid-catalyzed proton transfer to carbon, and appropriately resolvating them, W^r, has been recently estimated as about 8 kcal mol^{-1}, using Marcus' formulation.[26] The correspondence is just about what might be expected if we are, here, measuring the rate of a similar process for which W^r is the standard free energy.

The reprotonations of β-diketone anions[27,28] and cyanocarbon anions[29,30] have rate constants similar to those discussed here and may well use analogous mechanisms.

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Infrared and Raman Spectra of Gaseous and Matrix Isolated Beryllium Borohydride

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Abstract: Infrared spectra of gaseous and matrix isolated beryllium borohydride (BeB_2H_8, BeB_2D_8, and BeB_2HD_7) are presented. In addition Raman spectra have been recorded for the gas despite the low vapor pressure of ~10 mm and, in one of its first applications, Raman matrix isolation spectra were obtained. Depolarization measurements were made for both the gas and the matrix. The results indicate that two distinct structures of BeB_2H_8 coexist in equilibrium in the vapor phase. On cooling to 20°K *via* the matrix, the equilibrium shifts and only one form is trapped. Isotopic data and the Raman depolarization results are most consistent with a C_{3v} configuration which is obtained by distorting a D_{3d} structure so as to produce a double minimum for the Be atom. A frequency assignment is presented for this C_{3v} model and a brief discussion of the unusual bonding about the Be atom is given. The frequencies corresponding to the second form of gaseous BeB_2H_8 suggest the presence of a terminal BH_2 group and a double hydrogen bridge but do not allow a clear distinction between the classical D_{2d} structure and a triangular configuration.

The structure of gaseous beryllium borohydride, BeB_2H_8, continues to be a subject of some controversy. To date, no fewer than five different configurations (I–V in Figure 1) have been proposed, yet none can be viewed as established. Because of its volatility, BeB_2H_8 is classed as a covalent borohydride such as $Al(BH_4)_3$ and $Zr(BH_4)_4$. It was first prepared[1] in 1940 by the reaction of B_2H_6 and $Be(CH_3)_2$ and, from vapor density measurements, was found to exist as monomeric BeB_2H_8. In 1946 an electron diffraction experiment[2] was interpreted in terms of a triple hydrogen bridged D_{3d} model I but shortly thereafter, from an infrared study, Longuet-Higgins[3] suggested that a double bridged D_{2d} structure II was more reasonable. Reexamination[4] of the original electron diffraction data showed that such a model could be accommodated if the bridge bonds were highly asymmetrical.

Thus the D_{2d} structure was considered to be established until 1967 when the Oslo electron diffraction group repeated the experiment[5] and, surprisingly, found that their new data were not compatible with II but were consistent with a triangular C_{2v} structure III. Shortly thereafter mass spectroscopic and infrared results were reported[6] to favor a singly bridged triangular structure IV of C_2 symmetry. About the same time, we noted[7] that the vapor infrared vibration–rotation band contours were not those of a rigid rotor symmetric top (II) but were more consistent with III (or IV). We also reported a dipole moment of 2.1 ± 0.5 D from dielectric measurements. The existence of a substantial dipole moment was later confirmed by an electric deflection experiment.[8] However, it should be noted that several attempts[9] to obtain a microwave spectrum

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