

Let us consider for a moment a fictitious molecule of known geometry where the molecular motion of the hydrocarbon chain is completely frozen in. A Cartesian coordinate system is attached to each chain segment. Using appropriate transformation matrices of order 3, the projection of the  $i$ th bond vector along the axis of the first coordinate system is then found by stepwise transformations through  $i - 1$  foregoing coordinate systems. In the reference frame of the first bond eq 4 can therefore be expressed in the following form

$$\mathbf{r} = \sum_{i=1}^n (\mathbf{T}_1 \mathbf{T}_2 \dots \mathbf{T}_{i-1}) \mathbf{l}_i \quad (5)$$

(for  $i = 1$ ,  $\mathbf{T}_0$  is the identity matrix of order 3).

Let us now return to the problem of a flexible hydrocarbon chain in a lipid bilayer. In this case the average orientation of the vector has been found to be parallel to the bilayer normal.<sup>9</sup> Furthermore, each carbon-carbon bond can assume three conformations (trans, gauche<sup>+</sup>, gauche<sup>-</sup>) with rapid interconversions occurring between these conformational states. In order to determine the average length of the vector, the serial product of transformation matrices must be replaced by its statistical mechanical average.<sup>32</sup> Omitting details of this rather lengthy calculation<sup>31</sup> the final result can be expressed as follows. The average length of the carbon skeleton of caprylic acid (decanol) with the

chain aligned parallel to the bilayer normal amounts to 7.6 Å (9.1 Å). Addition of appropriate van der Waals radii for the terminal methyl protons and the carboxyl groups (hydroxyl group) increases the chain length to 9.1 Å (11.3 Å). Furthermore, it is known from studies with rigid steroid spin labels that the hydrocarbon chains are subjected to wobbling motions around the bilayer normal, the mean angular deviation being about 30°. Taking into account this overall motion reduces the projection of the chain on the direction of the bilayer normal to 8.5 Å (10.6 Å). The molecular ratio of decanol molecules to caprylic acid molecules in phase L<sub>1c</sub> is 1.02. The average length of all hydrocarbon chains therefore amounts to 9.52 Å. The total thickness of the bilayer is given by twice this length plus additional 2.4 Å for the van der Waals distance between the terminal methyl groups in the middle of the bilayer. The final result is a thickness of 21.4 Å, which is in fair agreement with a value of 21.7 Å determined by X-ray diffractions.<sup>15</sup> Using the same formalism we have analyzed five more sodium caprylate-decanol-water systems with varying bilayer thickness. In no case was the difference between the spin label data and the X-ray investigation larger than 2%.<sup>31</sup> These results are particularly satisfying because they lend additional support to the semiempirical approach used for describing the chain flexibility and because they give us some confidence to apply the same method to determine the dimension of unknown liquid crystalline bilayers.

(32) P. J. Flory, "Statistical Mechanics of Chain Molecules," Interscience, New York, N. Y., 1969, p 99.

## H<sub>2</sub>BH<sub>3</sub> as an Intermediate in Tetrahydridoborate Hydrolysis<sup>1</sup>

M. M. Kreevoy\* and J. E. C. Hutchins

Contribution from the Chemical Dynamics Laboratory, University of Minnesota, Minneapolis, Minnesota 55455. Received December 1, 1971

**Abstract:** The rate law corresponding to a simple, rate-determining, proton transfer fails to correlate rates of BH<sub>4</sub><sup>-</sup> hydrolysis in basic solutions. A rate law arising from a mechanism involving an intermediate which can react with OH<sup>-</sup> to regenerate BH<sub>4</sub><sup>-</sup> successfully correlates all the observed rate constants. Under appropriate conditions BH<sub>4</sub><sup>-</sup> exchanges hydrogen isotopes with the solvent. The exchange rate appears to be about half the rate of regeneration of BH<sub>4</sub><sup>-</sup> from the intermediate. These observations strongly suggest an intermediate of composition BH<sub>3</sub> but with the added proton equivalent to only one of the original four. It is isoelectronic with CH<sub>3</sub><sup>+</sup>, and a structure analogous to **1** is suggested.

The purpose of this paper is to firmly establish a number of key facts about the acid-catalyzed aqueous solution hydrolysis of tetrahydridoborate ion (BH<sub>4</sub><sup>-</sup>) and to develop a mechanism consistent with all the facts. The overall reaction is shown in eq 1. A number of authors<sup>2-6</sup> have shown that the

(1) Based on the Ph.D. Thesis of J. E. C. Hutchins, University of Minnesota, 1969; presented, in part, at the 155th National Meeting of the American Chemical Society, San Francisco, Calif., March 31-April 5, 1968.

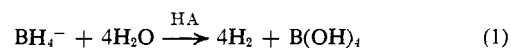
(2) J. A. Gardiner and J. W. Collat, *J. Amer. Chem. Soc.*, **87**, 1692 (1965).

(3) J. A. Gardiner and J. W. Collat, *Inorg. Chem.*, **4**, 1208 (1965).

(4) K. N. Mochalov and C. G. Gilmanchin, *Dokl. Akad. Nauk SSSR*, **132**, 134 (1960).

(5) R. E. Davis, E. B. Bromels, and C. L. Kibby, *J. Amer. Chem. Soc.*, **84**, 885 (1962).

(6) L. A. Levine and M. M. Kreevoy, *ibid.*, **94**, 3346 (1972).



release of H<sub>2</sub> is stepwise, and intermediates, BH<sub>4-n</sub>OH<sub>n</sub><sup>-</sup>, are involved, but the second and fourth hydrogen molecules are released considerably more rapidly than the first, so that the rate of the first step substantially determines the rate of the whole process. It has been generally,<sup>7</sup> but not universally,<sup>8</sup> supposed that the release of the first mole of H<sub>2</sub> from BH<sub>4</sub><sup>-</sup> was a one-step reaction involving a rate-determining proton transfer and having a rate law given by eq 2, which would be appro-

$$-d(\text{BH}_4^-)/dt = (\text{BH}_4^-) \sum_{\text{HA}} k_{\text{HA}} (\text{HA}) \quad (2)$$

(7) R. E. Davis and C. G. Swain, *ibid.*, **82**, 5949 (1960).

(8) R. E. Mesmer and W. L. Jolly, *Inorg. Chem.*, **1**, 608 (1962).

priate for such a reaction. Although there have been several reports that eq 2 fails in fairly basic solutions,<sup>5,9-11</sup> these have lacked quantitative authority and have been discounted as manifestations of electrolyte effects.<sup>5</sup> In the present paper conclusive evidence is provided that the actual rate falls systematically below the predictions of eq 2 at OH<sup>-</sup> concentration above 0.1 M, the discrepancy increasing with the base concentration to more than a factor of 10 in 1 M NaOH. It is shown to be very unlikely that this is an electrolyte effect.

The present paper also confirms an earlier report<sup>8</sup> that isotope exchange with the solvent accompanies hydrolysis when the solvent is D<sub>2</sub>O and the reaction medium is quite basic. It is shown that unreacted BH<sub>4</sub><sup>-</sup> takes up deuterium and that the uptake is stepwise, one deuterium at a time being taken up. Further, the rate of deuterium uptake approximates the discrepancy by which eq 2 overestimates the hydrolysis rate. All of this tends to suggest a hydrolysis mechanism which can produce exchange as a side reaction. It is definitely incompatible with the impurity-catalyzed mechanism<sup>12</sup> that had been suggested to explain the previous report of exchange without elaborating beyond a simple, one-step mechanism for the first step of the hydrolysis.

## Results and Discussion

Like previous investigators<sup>5,13-16</sup> we have found the hydrolysis to be first order in BH<sub>4</sub><sup>-</sup> over the whole range of conditions studied. Pseudo-first-order rate constants for hydrolysis are designated  $k_1^{\text{hydr}}$ . Replication under a variety of conditions indicated that an average deviation from the mean values of around 3% was associated with  $k_1^{\text{hydr}}$ , with individual deviations occasionally as high as 10%.

Because small traces of metallic impurities have been reported to have striking effects, both on the hydrolysis<sup>17</sup> and on the exchange<sup>12</sup> processes, the present work was done with very carefully purified materials, as described in the Experimental Section. In general, reaction solutions did not exceed 10<sup>-6</sup> M total transition metal concentration, and most of this surely must have been iron, which is not, itself, among the major offenders.<sup>12,17</sup> Further, in several experiments, involving both exchange and hydrolysis, impurities were deliberately allowed to be present at several times the usual concentration, either by using unpurified starting material or by adding ferrous ammonium sulfate. In no case was any discrepancy outside of the usual scatter noted. It is likely therefore that the present results are free of anomalies induced by metallic impurities.

(9) J. B. Brown and M. Svensson, *J. Sci. Lab., Denison Univ.*, **44**, 117 (1958).

(10) K. N. Mochalov, V. S. Khain, and G. G. Gil'manshin, *Dokl. Akad. Nauk SSSR*, **162**, 613 (1965).

(11) R. W. Bragdon, U. S. Patent 2,970,114 (1960); *Chem. Abstr.*, **55**, 19857f (1961).

(12) R. E. Davis, J. A. Bloomer, D. R. Casper, and A. Saba, *Inorg. Chem.*, **3**, 460 (1964).

(13) R. L. Pescok, *J. Amer. Chem. Soc.*, **75**, 2862 (1953).

(14) E. H. Jensen, "A Study on Sodium Borohydride with Special Reference to its Analytical Application in Organic Chemistry," *Nyt Fordisk Forlag, Arnold Busch, Copenhagen, Denmark*, 1954.

(15) J. B. Brown and M. Svensson, *J. Amer. Chem. Soc.*, **79**, 6581 (1957).

(16) W. H. Stockmayer, R. R. Miller, and R. J. Zeto, *J. Phys. Chem.*, **65**, 1076 (1961).

(17) H. I. Schlesinger, H. C. Brown, A. E. Finholt, J. R. Gilbreath, H. R. Hoekstra, and E. K. Hyde, *J. Amer. Chem. Soc.*, **75**, 215 (1953).

**Electrolyte Effect on Hydrolysis.** Previous work has indicated that added NaCl has only small effects on  $k_1^{\text{hydr}}$  at constant (OH<sup>-</sup>).<sup>5</sup> This has now been confirmed and extended to NaBr and NaSCN.<sup>18</sup> The effects are not larger than 30% for any of these salts at electrolyte concentrations up to 3 M. This relative insensitivity is expected. The rate constant,  $k_1^{\text{hydr}}$ , has both H<sup>+</sup> catalyzed and uncatalyzed (water-catalyzed) components. The H<sup>+</sup> catalyzed component is given by  $K_w k_H \gamma_{\text{BH}_4^-} / (\text{OH}^-) \gamma_{\text{OH}^-} \gamma^\ddagger$ , where  $K_w$  is the autoprotolysis constant of water and  $k_H$  is the catalytic coefficient of H<sup>+</sup>, both in infinitely dilute, aqueous solution.<sup>19</sup> The  $\gamma$ 's are activity coefficients. Since the transition state is formally neutral, the ratio of activity coefficients is unity in the approximation that  $\gamma$  is unity for all neutral species and the same for all anions. This approximation is supported for sodium salts by the near identity of their mean ion activity coefficients in the 1-3 M concentration range.<sup>20</sup> The rate coefficient for the uncatalyzed (water-catalyzed) portion of  $k_1^{\text{hydr}}$  is given by  $k_{\text{H}_2\text{O}} \gamma_{\text{BH}_4^-} \gamma_{\text{H}_2\text{O}} / \gamma^\ddagger$ . Since this transition state is negatively charged, as indicated, the ratio of activity coefficients is again expected to be unity. It therefore appears that activity coefficients can be neglected with errors that do not exceed ~30% even in 3 M electrolyte if  $K_w / (\text{OH}^-)$ , hereafter called  $\eta$ , is used as the measure of acidity. This generalization remains true, for the reasons given, even in the more complicated rate laws discussed below.

**Effect of Acidity on Hydrolysis Rate.** In H<sub>2</sub>O at 25.0° 36  $k_1^{\text{hydr}}$  values were determined at 13 different (OH<sup>-</sup>) ranging from  $7.57 \times 10^{-4}$  to 2.27 M. At (OH<sup>-</sup>) below 0.1 M  $k_1^{\text{hydr}}$  is a linear function of  $\eta$  with non-zero intercept, as previously reported.<sup>5</sup> Above that concentration, however, deviations are increasingly apparent, reaching a factor of more than 10 at the highest base concentration. The situation is shown graphically in Figure 1. The experimental results are in good agreement with those of Davis, Bromels, and Kibby,<sup>5</sup> as shown in the figure, but these workers appear to have lacked confidence in results obtained in strongly basic solution. Nevertheless, a commercial product (Stabilized Sodium Borohydride) appears to be based on such deviations.<sup>11</sup> As shown above, these deviations are far outside reasonable limits of combined electrolyte effects and experimental error. Since the conventional mechanism<sup>7</sup> is unable to accommodate this behavior, it cannot be correct.

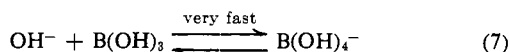
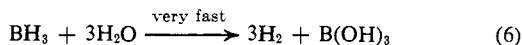
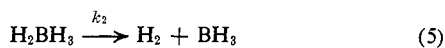
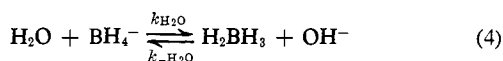
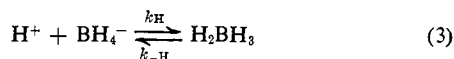
A mechanism which will accommodate the dependence of  $k_1^{\text{hydr}}$  on  $\eta$  was originally proposed by Bell<sup>21</sup> for the hydrolysis of diazoacetate. It is shown in eq 3-7, as specialized for the case of BH<sub>4</sub><sup>-</sup> hydrolysis in aqueous base. An intermediate is required in this mechanism, and it is not likely to be the well-known intermediate, BH<sub>3</sub>OH<sup>-</sup>, because the latter cannot react with OH<sup>-</sup> to regenerate BH<sub>4</sub><sup>-</sup>. An intermediate with composition BH<sub>5</sub> meets all the requirements. It is written H<sub>2</sub>BH<sub>3</sub> rather than BH<sub>3</sub> because hydrolysis of BD<sub>4</sub><sup>-</sup> in H<sup>-</sup>-H<sub>2</sub>O gives ~95% of HD, indicating that the incoming proton becomes equivalent to only

(18) We are indebted to Miss Linda Levine for these measurements.

(19) J. N. Bronsted, *Z. Phys. Chem.*, **102**, 169 (1922).

(20) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold, New York, N. Y., 1967, pp 731-735.

(21) R. P. Bell, "The Proton in Chemistry," Methuen, London, 1959, p 135.



one of the hydride hydrogens.<sup>22</sup> If  $k_2$  is much larger than  $k_{-H}$ , then  $k_1^{\text{hydr}}$  should be given, over the whole range of  $(\text{OH}^-)$ , by eq 8.<sup>21,23</sup> The mechanistic significance

$$k_1^{\text{hydr}} = \frac{k_H \eta^2 + k_{H_2O} \eta}{\eta + K_w k_{-H_2O} / k_2} \quad (8)$$

of eq 3–8 is that the reaction is of the A-SE2 type in more acidic (less basic) solutions but goes over to the A-1 type in more basic solution.<sup>23</sup> Equation 8 is clearly of the proper form at the extrema. The data were fitted to eq 8 by adjusting the three parameters  $k_H$ ,  $k_{H_2O}$ ,  $k_{-H_2O}/k_2$  so as to minimize  $\{(k_1^{\text{hydr}} - k_1^{\text{calcd}})/k_1^{\text{hydr}}\}^2$ , where  $k_1^{\text{calcd}}$  is the right-hand side of eq 8.<sup>24</sup> The resulting parameters, which are given in Table I, reproduce the data for  $(\text{OH}^-) <$

Table I. Rate Parameters at 25°

Parameter	Unit	Value <sup>a,b</sup>
$k_H$	$M^{-1} \text{sec}^{-1}$	$9.9 \pm 0.3 \times 10^5$
$k_D$	$M^{-1} \text{sec}^{-1}$	$5.3 \pm 0.4 \times 10^5$
$k_{H_2O}$	$\text{sec}^{-1}$	$2.2 \pm 0.2 \times 10^{-7}$
$k_{D_2O}$	$\text{sec}^{-1}$	$2.4 \pm 0.3 \times 10^{-8}$
$k_{-H_2O}/k_2$	$M^{-1}$	$2.3 \pm 0.3$
$k'_{-D_2O}/k'_2$	$M^{-1}$	$1.9 \pm 0.4$

<sup>a</sup> These values are approximations of infinite dilution values, as discussed in the text. <sup>b</sup> The uncertainties are standard deviations,  $\sigma$ . <sup>c</sup> Both primed quantities are actually sums; discussed in the text.

0.1  $M$  (26 pts) with an average deviation of 7% and that for  $(\text{OH}^-) > 0.1 M$  (10 pts) with an average deviation of 17%. The former is only a little larger than the experimental imprecision and the latter is entirely consistent with the neglected residual electrolyte effects. The fit of eq 8 to the high-base data is shown graphically in Figure 1.

An analogous study was carried out in  $\text{D}_2\text{O}$ , with six measurements of  $k_1^{\text{hydr}}$  in  $\text{NaOD} < 0.1 M$  and 12 in  $\text{NaOD} > 0.1 M$ , the highest being 2.51  $M$ . After these experiments the H content of the solvent was determined,<sup>25</sup> the values ranging from 0.6 to 1.8%. The most important effect of this H is on the autoprotolysis constant of the water, which determines  $\eta$ . In each case an autoprotolysis constant appropriate to the actual isotopic composition of the solvent was used.<sup>26</sup> The rate constants themselves were not corrected, as

(22) (a) W. L. Jolly and R. E. Mesmer, *J. Amer. Chem. Soc.*, **83**, 4470 (1961); (b) P. R. Girardot and R. W. Parry, *ibid.*, **73**, 2368 (1951).

(23) M. M. Kreevoy and D. E. Konasewich, *J. Phys. Chem.*, **74**, 4464 (1970).

(24) The minimizations referred to in this paper were carried out on several digital computers. We are grateful to Dr. M. Nakashima and Dr. E. Anderson for programming and other help with the computation and to the Numerical Analysis Center of the University of Minnesota for a gift of computer time.

(25) M. M. Kreevoy and T. S. Straub, *Anal. Chem.*, **41**, 214 (1969).

(26) V. Gold, *Advan. Phys. Org. Chem.*, **7**, 259 (1971).

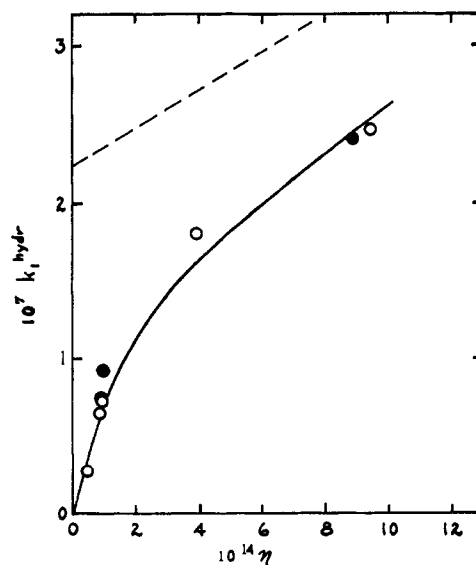


Figure 1. Hydrolysis rate as a function of acidity in 0.1–2.3  $M$   $\text{NaOH}$ . The open points are new results. Several of them represent the average of a number of determinations, so that ten values of  $k_1^{\text{hydr}}$  are actually represented. Closed points represent several of the values of Davis, Bromels, and Kibby.<sup>5</sup> The solid line represents the predictions of eq 8. The dashed line is the prediction of eq 2, using the presently determined values of  $k_H$  and  $k_{H_2O}$ .

such a correction would in no case have amounted to as much as 2%.

The standard deviations ( $\sigma$ ) given in Table I were estimated in the usual way, taking into account the strong correlation between  $k_{H_2O}$  and  $k_{-H_2O}/k_2$  and between  $k_{D_2O}$  and  $k'_{-D_2O}/k'_2$ .<sup>27</sup> (That is,  $k_{H_2O}$  can be increased if  $k_{-H_2O}/k_2$  is simultaneously decreased with relatively little damage to the fit.)

Values of  $k_H$  have been previously reported by a number of authors and are tabulated by Gardiner and Collat.<sup>2</sup> Even apart from a discredited value of 0.77 they range from  $2.5 \times 10^5$  to  $2.3 \times 10^6 M^{-1} \text{sec}^{-1}$ . Much of the discrepancy is more apparent than real, however, arising from the use of different ionic strengths and different methods of treating electrolyte effects. For example, the  $k_1^{\text{hydr}}$  values of Davis, Bromels, and Kibby<sup>5</sup> appear to be in good agreement with values obtained in the present work under comparable conditions as shown in Figure 1. These authors report a value of  $1.00 \times 10^6 M^{-1} \text{sec}^{-1}$  for  $k_H$  at an ionic strength of 0.1, apparently based, however, on the use of  $-\text{antilog pH}$  as the acidity function, rather than  $\eta$ . They give  $2.3 \times 10^6 M^{-1} \text{sec}^{-1}$  as the value appropriate to infinite dilution. For reasons given in the section on electrolyte effects we believe our present parameter values should be good approximations to infinite dilution values. The Davis, Bromels, and Kibby extrapolation to infinite dilution appears to neglect the fact that  $\gamma_{\text{H}^+}$  is already included in  $\text{pH}$  and also to overestimate the deviation of  $\gamma_{\text{BH}_4^-}$  from unity by using the Debye–Hückel limiting law in solutions of finite concentration. Values of  $10^{-7} \text{sec}^{-1}$ <sup>5,28</sup> and  $6 \times 10^{-6} \text{sec}^{-1}$ <sup>2,28</sup> have been given for  $k_{H_2O}$  at 25°. Their authors clearly intend them to be rough estimates

(27) J. Topping, "Errors of Observation and Their Treatment," Chapman and Hall, London, 1962, pp 17, 62, 105–109.

(28) Actually both previous papers<sup>5,28</sup> give second-order rate constants for reaction with water. We have regenerated  $k_{H_2O}$  from them by multiplying by 55.

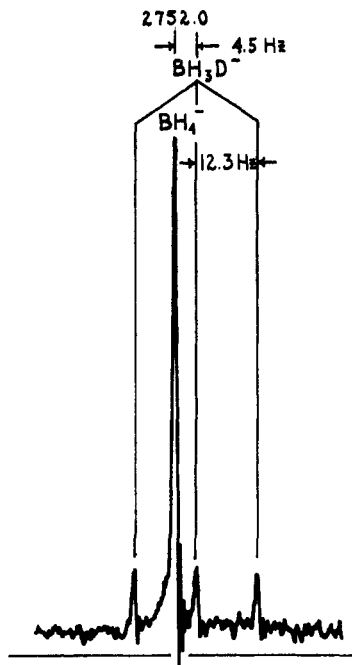
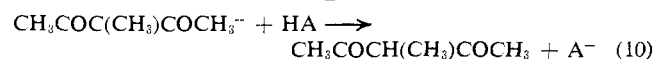
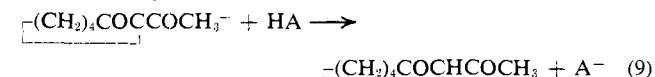


Figure 2. The  $^{11}\text{B}$  nmr spectrum of a solution in  $\text{D}_2\text{O}$ , originally 1  $M$  in  $\text{NaBH}_4$  and 1  $M$  in  $\text{NaOD}$ , which had been allowed to react at  $25^\circ$  for 2 years. The spectrum was made at 32.1 MHz with  $^1\text{H}$  noise decoupling. The position of the  $\text{BH}_4^-$  line is given relative to  $\text{BF}_3$  etherate in an external capillary. The spectrum was recorded by W. C. Jankowski of Varian.

only. A value of  $10^{-7} \text{ sec}^{-1}$  can be obtained by extrapolation from temperatures around  $75\text{--}100^\circ$ .<sup>8</sup> They all suffer from the failure to take into account the non-linear behavior of  $k_1^{\text{hydr}}$  as a function of acidity in solutions of pH higher than 12. The third parameter,  $k_{-\text{H}_2\text{O}}/k_2$ , has not been previously identified or evaluated.

**Isotope Effect.** Table I furnishes  $k_{\text{H}}/k_{\text{D}}$  ( $1.9 \pm 0.2$ ) and  $k_{\text{H}_2\text{O}}/k_{\text{D}_2\text{O}}$  ( $9 \pm 2$ ). The former has been previously reported by Davis and coworkers<sup>5</sup> who originally gave 4.9 or 3.0, depending on the method of measurement, and later gave 1.3 as a corrected value;<sup>12</sup> and also by Mesmer and Jolly,<sup>8</sup> who give 1.56. The latter authors do not give a quantitative measure of their uncertainty, but it appears to be about 10% in each of the two parameters. They also do not report verification of the deuterium content of their reactions mixtures in " $\text{D}_2\text{O}$ ." Given these uncertainties the Mesmer and Jolly value is probably not significantly different from the present one. The original values of Davis and Kibby are now thought to have been systematically in error because of impurity effects. It is impossible to determine the quantitative reliability of the more recent value, which is given only as a footnote.<sup>12</sup>

The two isotope effects are consistent with rate-determining proton transfers. The difference between them is striking but not unprecedented. The reactions shown in eq 9 and 10,<sup>29,30</sup> which have rate constants



(29) T. Riley and F. A. Long, *J. Amer. Chem. Soc.*, **84**, 522 (1962).

(30) F. A. Long and D. Watson, *J. Chem. Soc.*, 2019 (1958).

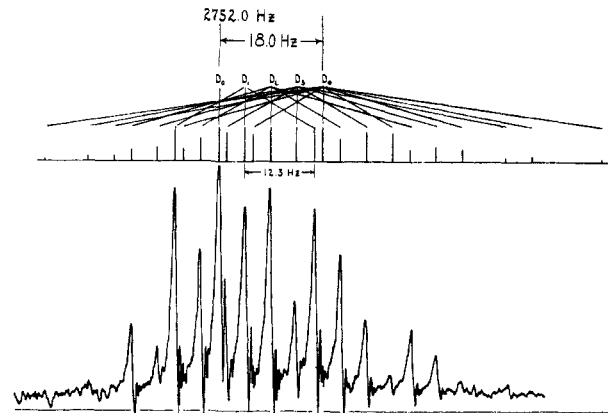


Figure 3. The  $^{11}\text{B}$  nmr spectrum of a solution in  $\text{D}_2\text{O}$ , originally 4.4  $M$  in  $\text{NaOD}$  and 1  $M$  in  $\text{NaBH}_4$ , which had been allowed to react at  $100^\circ$  for 1 month. The spectrum was made at 32.1 MHz with  $^1\text{H}$  noise decoupling. The position of the  $\text{BH}_4^-$  line is given relative to  $\text{BF}_3$  etherate in an external capillary. The stick diagram gives the position and relative intensity of the lines expected in the first-order spectrum of each species. The most intense line of each species was made equal, without regard for the relative abundance of the species, which is not exactly known. The spectrum was recorded by W. C. Jankowski of Varian.

in the same range as the present reaction, show isotope effects of around 1.5 when HA is the aquated proton and around 6 when it is acetic acid. Detailed discussion of these isotope effects has been given elsewhere.<sup>6</sup>

**Exchange.** Uptake of deuterium by unhydrolyzed  $\text{BH}_4^-$  in basic  $\text{D}_2\text{O}$  at both  $25$  and  $100^\circ$  is unambiguously shown by the  $^{11}\text{B}$  nmr spectra of interrupted reaction mixtures (Figures 2 and 3).  $^1\text{H}$  nmr spectra are also uniquely consistent with these conclusions.<sup>31</sup> These spectra also show that the deuterium is taken up stepwise, one atom at a time. This is not explainable by an impurities-catalyzed reaction, as that reaction does not lead to exchange in the starting material.<sup>12</sup> Also, the impurities-catalyzed mechanism involves reactive intermediates in which multiple exchange would be expected,<sup>12</sup> so that, if it were somehow modified so as to account for the formation of deuterated starting material, one would expect multiple substitutions in each step. These observations are, however, quite compatible with eq 3-5.

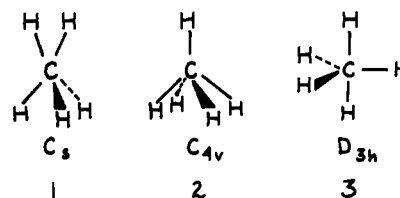
If the hydrolysis is carried out in  $\text{D}_2\text{O}$  the intermediate is  $\text{HDBH}_3$ . This may either lose HD, resulting in hydrolysis, lose  $\text{H}^+$ , resulting in exchange, or lose  $\text{D}^+$ , resulting in no observable reaction. The sum of all three rates, which is equal to the rate of formation of  $\text{HDBH}_3$  since the latter does not build up, should be given by  $(k_{\text{D}\eta\text{D}} + k_{\text{D}_2\text{O}})(\text{BH}_4^-)$ , where the rate constants are those given in Table 1. Since all the  $\text{HDBH}_3$  which does not hydrolyze undergoes either  $\text{H}^+$  removal or  $\text{D}^+$  removal, the sum of these two rates is given by the difference between  $(k_{\text{D}\eta\text{D}} + k_{\text{D}_2\text{O}})(\text{BH}_4^-)$  and  $k_1^{\text{hydr}}(\text{BH}_4^-)$ . The exchange rate is probably a little over a half of this difference, since the rate of abstraction of  $\text{D}^+$  from so reactive an intermediate must nearly equal the rate of abstraction of  $\text{H}^+$ . Using the parameters given in Table 1,  $(k_{\text{D}\eta\text{D}} + k_{\text{D}_2\text{O}}) - k_1^{\text{hydr}}$  for 1  $M$   $\text{OD}^-$  in  $\text{D}_2\text{O}$  is  $1.6 \times 10^{-8} \text{ sec}^{-1}$ , and half of this is  $0.8 \times 10^{-8} \text{ sec}^{-1}$ . The apparent rate

(31) J. E. C. Hutchins, Ph.D. Thesis, University of Minnesota, 1969, pp 80, 87.

constant for exchange can be estimated from Figure 2 if  $\text{BH}_4^-$  and all the deuterated species are assumed to hydrolyze at the same rate. (Not much hydrolysis had occurred in any event. The sample still showed over 70% of its original reducing capacity.) The rate constant is  $(1/t) \ln \{[(\text{BH}_4^-) + (\text{BH}_3\text{D}^-)]/(\text{BH}_4^-)\}$  where  $t$  is the time in which reaction has occurred (2 years). Substitution of appropriate numerical values, using the intensities taken from Figure 2 for the relative concentrations of the boron species gives  $0.5 \times 10^{-8} \text{ sec}^{-1}$ . This is surely an underestimate since it neglects multiply deuterated species, whose signals could not be separated from the noise at this low level of deuteration, but which Figure 3 shows must be present. Taking this and the general quantitative unreliability of any "one point rate constant" into account, the agreement with the prediction of the mechanism must be considered entirely satisfactory and to give further support to that mechanism.

Jolly and Mesmer<sup>22</sup> have reported a pH-independent hydrogen exchange for  $\text{BH}_4^-$  in  $\text{D}_2\text{O}$  containing 1–5  $M$   $\text{OD}^-$  at temperatures between 70 and 100°, and a  $\text{D}^+$  catalyzed exchange in  $\text{D}_2\text{O}$  of "pH" between 7 and 9. The exchange is faster than hydrolysis in the strongly basic solutions, but the exchange rate is only 6% of the hydrolysis rate at the higher "pH's." These results have been discounted as attributable to impurities,<sup>12</sup> but, qualitatively, we have reproduced them, and they fit nicely into the mechanism shown in eq 3–7. In very basic solution the most important acid becomes the water, so the rate of protonation becomes nearly independent of the acidity or basicity of the medium. In such solutions most of the  $\text{H}_2\text{BH}_3$  (or its isotopic analog) reverts to chemically unreacted  $\text{BH}_4^-$ , so that the rate of exchange is almost equal to the rate of protonation of  $\text{BH}_4^-$  (which is independent of the acidity of the medium). In more acid solution the most important acid is  $\text{H}^+$ , and the rate of protonation is directly proportional to its concentration. In such solutions the most important reagent which would abstract a proton to give exchange would be water (eq 3 from right to left). The rate of such a reaction is pH independent, as is loss of  $\text{H}_2$  from  $\text{H}_2\text{BH}_3$  (eq 5) so the fractionation between these two paths would be pH independent, and the rate of exchange would be a constant fraction of the protonation rate. In this case that fraction is small, which supports our neglect of  $k_{-H}$  by comparison with  $k_2$ .

**Structure of the Intermediate.**  $\text{H}_2\text{BH}_3$  is isoelectronic with  $\text{CH}_5^+$ , and it is likely that they have similar structures.  $\text{CH}_5^+$  is an important species in mass spectroscopy,<sup>32</sup> and recent evidence suggests that it is also an intermediate in certain solution reactions in very strong acid.<sup>33,34</sup> A good deal of theoretical work has recently been devoted to its structure,<sup>33–36</sup> which seems to be **1**, although **2** and **3** may not be much less stable. The boron analog of **1** is entirely satisfactory in ratio-



nalizing the hydrolytic behavior of  $\text{BH}_4^-$ . The analog of **3** is incompatible with the observation<sup>22</sup> that hydrolysis of  $\text{BD}_4^-$  in  $\text{H}^+ - \text{H}_2\text{O}$  gives  $\sim 95\%$   $\text{HD}$ . **3** would give large amounts of  $\text{D}_2$  under those conditions. The analog of **2** can be made satisfactory if it is specified that the apical proton is the one added from solution and is always part of any  $\text{H}_2$  molecule lost, and other structures can also be postulated which seem to be in accord with the available evidence. However, the analog of **1** seems plausible and we know of no reason to go beyond it at this time. We also cannot distinguish between a structure like **1** and one in which the incoming proton is nonequivalent with the hydridic proton but exchanges places with it very rapidly (a fluctuating ion pair). Such a structure becomes kinetically equivalent to **1** if a number of exchanges take place prior to further reaction.

## Conclusion

It can be concluded that hydrolysis of  $\text{BH}_4^-$  and its exchange of hydrogen isotopes with the protons of an aqueous solvent both pass through an intermediate of composition  $\text{BH}_5$ , probably having a structure analogous to **1**. It seems entirely likely that analogous intermediates are also involved in the various exchange and hydrolysis reactions of trihydridocyanoborate<sup>37</sup> and amine-boranes.<sup>38,39</sup> These conclusions are also supported by recent work of Olah and coworkers.<sup>40</sup>

## Experimental Section

**Materials.**  $\text{NaBH}_4$  was obtained from Alfa Inorganics, Inc. As received it showed about 95% of the theoretical reducing power. It was dried for 15 hr at 100° under vacuum and then as much as possible was dissolved in ten times its own weight of anhydrous bis-(2-methoxyethyl) ether at 45°. (Its solubility is maximized at that temperature.<sup>41</sup>) The mixture was filtered and the  $\text{NaBH}_4$  was caused to precipitate by addition of five times its weight of ether. This material was collected and dried for 15 hr at 56° and for 1 hr at 190°, all under vacuum. The resulting material showed no marked improvement in its reducing power, but an 0.1  $M$  solution of the purified material in water showed only  $\sim 2 \times 10^{-7} M$  of transition metal impurities, about one-seventh of the original level.

Sodium hydroxide (Allied Chemical Co., Analytical Reagent Grade) was made into a saturated solution with purified water. More dilute solutions were prepared by removing supernatant solution from the precipitated  $\text{NaCO}_3$  and diluting with more purified water. A 1  $M$  solution prepared in this way showed  $7 \times 10^{-7} M$  of transition metal impurities.

Concentrated  $\text{NaOD}$  was prepared by dropping sodium metal into purified  $\text{D}_2\text{O}$  in a nitrogen atmosphere. A 1  $M$  solution made by diluting this material with ordinary purified water showed  $3 \times 10^{-7} M$  of transition metal impurities.

(37) M. M. Kreevoy and J. E. C. Hutchins, *J. Amer. Chem. Soc.*, **91**, 4329 (1969).

(38) R. E. Davis, A. E. Brown, R. Hopmann, and C. L. Kibby, *ibid.*, **85**, 487 (1963).

(39) H. C. Kelly, F. R. Marchelli, and M. B. Giusto, *Inorg. Chem.*, **3**, 431 (1964).

(40) G. A. Olah, P. W. Westerman, Y. K. Mo, and G. Klopman, *J. Amer. Chem. Soc.*, in press; we are grateful to Professor Olah for communicating his results to us prior to publication.

(41) Anonymous, "Sodium Borohydride," Ventron Corp., Beverly, Mass., 1966, p 6.

(32) V. Aguilanti and G. G. Volpi, *J. Chem. Phys.*, **44**, 2307 (1966); many earlier references are given in this paper.

(33) G. A. Olah, G. Klopman, and R. H. Schlosberg, *J. Amer. Chem. Soc.*, **91**, 3261 (1969).

(34) H. Hogeveen and C. J. Gaasbeek, *Recl. Trav. Chim. Pays-Bas*, **87**, 319 (1968).

(35) W. A. Lathan, W. J. Hehre, and J. A. Pople, *J. Amer. Chem. Soc.*, **93**, 808 (1971).

(36) W. Th. A. M. Van der Lugt and P. Ros, *Chem. Phys. Lett.*, **4**, 389 (1969).

Water was first deionized, then distilled, and then finally redistilled at a rate of 10 ml min<sup>-1</sup> from a 3-l. flask through a column 30 cm high and 6 cm wide, designed to minimize the carry over of water droplets. Transition metal impurities were less than 10<sup>-7</sup> M (the limit of sensitivity of the analytical method) in this water.

D<sub>2</sub>O was obtained from Bio-Rad Laboratories, Inc. It was reported to be 99.87 atom % D. A small scale version of the distillation described for water was used to lower the level of transition metal impurities to 2 × 10<sup>-7</sup> M.

Both H<sub>2</sub>O and D<sub>2</sub>O were freed from CO<sub>2</sub> after the final distillation and then protected from the atmosphere in the usual way.<sup>42</sup>

**Methods.** Rates were measured manometrically, using a modified version of the compensated manometer originally described by Moelwyn-Hughes and Johnson.<sup>43,44</sup> A supersaturated H<sub>2</sub> solution was prepared in this manometer by allowing a reaction to proceed for 15 hr without stirring. When stirring was begun, a 6-min half-life was observed for approach to equilibrium. In the present study the fastest reactions studied had half-lives of a number of hours. The slower ones, on which the more important conclusions are based, had half-lives of months or years.

Most of the rates were determined by a zeroth-order technique, as follows. After the reaction mixture was made up it was allowed to stand for 0.01–0.1 half-life to allow the reactions represented by eq 6 to reach a steady state. The rate of H<sub>2</sub> evolution was then

(42) I. M. Kolthoff and E. B. Sandell, "A Textbook of Quantitative Inorganic Analysis," Macmillan, New York, N. Y., 1963, p 527.

(43) E. A. Moelwyn-Hughes and P. Johnson, *Trans. Faraday Soc.*, **36**, 949 (1940).

(44) Reference 31, pp 26–28.

determined over a period of several hours or days. The BH<sub>4</sub><sup>-</sup> concentration was determined iodometrically. From this information, the known dimensions of the manometer and the solubility of H<sub>2</sub> in water, the rate of hydrolysis could be determined.<sup>31</sup> In solutions where both methods were usable, the zeroth-order technique gave results undistinguishable from those obtained by the more common first-order technique.<sup>45</sup> The rates of reactions with half-lives of up to 2 years could be conveniently determined by the zeroth-order technique.

The hydride content of solutions was determined iodometrically,<sup>46</sup> the standard method being modified to handle smaller quantities of material by a general reduction in scale.<sup>31</sup>

Transition metal concentrations were determined using the strong visible absorption of the 1,10-phenanthroline complexes, as suggested by Fortune and Mellon,<sup>47</sup> but substituting spectrophotometric detection using 10-cm cells for visual estimation of color intensity.

Acid and base concentrations were determined in the usual ways with constant boiling HCl as the ultimate standard.<sup>48</sup>

**Acknowledgment.** We are pleased to acknowledge the financial support of the National Science Foundation through GP-4915 and GP-13172.

(45) A. A. Frost and R. G. Pearson, "Kinetics and Mechanisms," 4th ed, Wiley, New York, N. Y., 1965, p 29.

(46) D. A. Lyttle, E. H. Jenson, and W. A. Struck, *Anal. Chem.*, **24**, 1843 (1952).

(47) W. B. Fortune and M. G. Mellon, *Ind. Eng. Chem., Anal. Ed.*, **10**, 60 (1937).

(48) A. I. Vogel, "A Textbook of Quantitative Inorganic Analysis," Longmans, Green and Co., London, 1939, p 279.

## Silicon-29 Chemical Shifts of Organosilicon Compounds<sup>1a</sup>

Roger L. Scholl, Gary E. Maciel,\*<sup>1b</sup> and W. Kenneth Musker

*Contribution from the Department of Chemistry, University of California, Davis, California 95616. Received January 13, 1972*

**Abstract:** One hundred and twenty natural abundance <sup>29</sup>Si resonances have been determined for neat liquid organosilicon compounds. The problems of weak signals and poor resolution were effectively dealt with by storing repetitive, frequency-stabilized, slow-passage, absorption-mode, proton-decoupled spectra in a computer of average transients, using a <sup>19</sup>F-locked spectrometer operating at 19.9 MHz for <sup>29</sup>Si. The empirical trends in the chemical shifts, which cover a range of 70 ppm, are discussed. Roughly constant, additive contributions to the <sup>29</sup>Si magnetic shielding are observed for a wide variety of substituents on silicon. The <sup>29</sup>Si shielding appears to be moderately insensitive to changes in substituents β to silicon in substituted tetramethylsilanes. The observed effects of saturated carbon atoms α, β, and γ to silicon on the <sup>29</sup>Si shieldings are comparable to the observed effects on <sup>13</sup>C, <sup>31</sup>P, and <sup>14</sup>N shieldings. The <sup>29</sup>Si shieldings in a series of substituted phenylsilanes correlate well with Hammett σ constants. Oxygen appears to transmit substituent effects more readily than either a CH<sub>2</sub> or a Si(CH<sub>3</sub>)<sub>2</sub> group. Silicon incorporated in hydrocarbon ring compounds shows decreased shielding with decreasing ring size, in contrast to <sup>13</sup>C shielding in similar compounds. Two resonances were observed for the different configurations of the diastereomeric compound (±)-methylphenyl(-)-menthoxyisilane. Qualitative observations of widely varying signal intensities were made which were evidently due to widely varying <sup>29</sup>Si relaxation times and <sup>29</sup>Si-<sup>1</sup>H nuclear Overhauser effects, with the latter leading to inverted signals for many compounds. The intrinsic solvent shifts of the <sup>29</sup>Si, <sup>13</sup>C, and <sup>1</sup>H resonances of tetramethylsilane as solute in pyridine and 14 substituted benzene and cyclohexane solvents have been determined with respect to pure TMS. The solvent shifts of <sup>29</sup>Si cover a range of 0.64 ppm.

To date only three studies involving the direct observation of <sup>29</sup>Si resonances have appeared in the literature. In 1956, and 1962, Lauterbur *et al.*,<sup>2</sup> reported

(1) (a) Supported by National Science Foundation Grants GP-8518 and 20523. (b) Correspondence regarding this article should be addressed to G. E. Maciel, Department of Chemistry, Colorado State University, Fort Collins, Colo. 80521.

(2) G. R. Holzman, P. C. Lauterbur, J. H. Anderson, and W. Koth, *J. Chem. Phys.*, **25**, 172 (1956); (b) P. C. Lauterbur, "Determination of Organic Structures by Physical Methods," Vol. 2, F. C. Nachod and W. D. Phillips, Ed., Academic Press, New York, N. Y., 1962, Chapter 7.

chemical shifts for about 50 compounds: in 1968 Hunter and Reeves<sup>3</sup> reported a systematic study of the series of compounds X<sub>n</sub>SiY<sub>4-n</sub>, where Y = CH<sub>3</sub>, X = OCH<sub>3</sub>, OC<sub>2</sub>H<sub>5</sub>, OCOCH<sub>3</sub>, H, C<sub>6</sub>H<sub>5</sub>, F, and Cl, plus chemical shifts for 15 miscellaneous compounds. These data have served to delineate the basic trends in the <sup>29</sup>Si chemical shifts of molecules with atoms of widely different electronegativity bonded to the silicon.

(3) B. K. Hunter and L. W. Reeves, *Can. J. Chem.*, **46**, 1399 (1968).