

tored are indicated in Tables I and II. In all cases, infinity spectra matched those of authentic product mixtures.

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## References and Notes

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## Hydrolysis Mechanism of $\text{BH}_4^-$ in Moist Acetonitrile<sup>1</sup>

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**Abstract:** Acetonitrile solutions containing up to 0.6 M  $\text{H}_2\text{O}$  do not hydrolyze  $\text{BH}_4^-$  measurably over a period of days. However,  $10^{-3}$  M  $\text{CF}_3\text{SO}_3\text{H}$  in acetonitrile completely hydrolyzes  $\text{BH}_4^-$  in less than 10 s. The hydrolysis of  $\text{BH}_4^-$  in acetonitrile containing acetic acid is first order in  $\text{BH}_4^-$ , and the apparent first-order constant  $k_1$  is given by  $k_1 = [k_0 + k_{\text{H}_2\text{O}}(\text{H}_2\text{O})] [K(\text{CH}_3\text{COOH})/1 + K(\text{CH}_3\text{COOH})]$  where  $K$  is the equilibrium constant for the formation of a complex between acetic acid and  $\text{BH}_4^-$ . It has a value of  $1.6 \pm 0.3 \times 10^2$ . This suggests the rate-determining step involves breakdown of the complex by an unpromoted and a water-promoted route at competitive rates. Acceleration by a tertiary amine suggests that the latter path involves nucleophilic attack by water on the complex.  $^{11}\text{B}$  NMR shows no exchange of H for D on boron in interrupted reactions using  $\text{D}_2\text{O}$  in place of  $\text{H}_2\text{O}$ , indicating the acetate ion remains firmly attached to one proton until the complex undergoes reaction. The complex is a rare example of a hydrogen bond not involving either unpaired electrons or a  $\pi$  bond. These observations are consistent with the existence of  $\text{BH}_5$  as an intermediate in the hydrolysis of  $\text{BH}_4^-$  in water, but some differences are apparent.

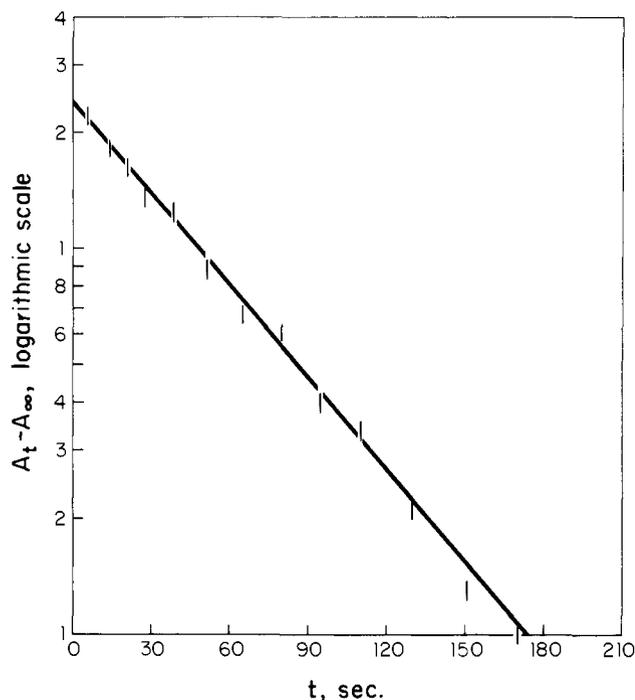
The hydrolysis of  $\text{BH}_4^-$  in aqueous solution apparently involves  $\text{BH}_5$  as an intermediate<sup>2</sup> with water acting as a proton relay.<sup>3</sup> In accordance with this conclusion, the proton catalytic coefficient,  $k_{\text{H}^+}$ , is lower in dimethyl sulfoxide ( $\text{Me}_2\text{SO}$ ) than in water by a factor of  $10^6$ .<sup>4</sup> The purpose of the present work was to compare acetonitrile (AN) with water and  $\text{Me}_2\text{SO}$  as solvents. Like  $\text{Me}_2\text{SO}$ , AN is a nonhydroxylic solvent, so it should be incapable of functioning as a relay for the proton or as a hydrogen bond donor. Unlike  $\text{Me}_2\text{SO}$ , it is also a poor hydrogen bond acceptor,<sup>5</sup> which should reduce the energy required to break solvent bonds to the proton. This work will provide some insight into the effect of these structural parameters on the mechanism.

## Experimental Section

**Materials.** Acetonitrile (99%) was obtained from the Aldrich Chemical Co. The only detectable impurity was water. Unpurified solvent and acetonitrile which had been dried by the method of Coetzee<sup>6</sup> gave indistinguishable rates. In most experiments the solvent was used as supplied and analyzed for water during the course of the experiment. Tetraethylammonium tetrahydridoborate ("borohydride") was obtained from the Ventrone Corporation and was used without further purification.  $N,N,N',N''$ -Pentamethyldiethylenetriamine (PMDETA) was obtained from Ames Laboratories and was redistilled under vacuum.  $\beta$ -Nicotinamide adenine dinucleotide ( $\text{NAD}^+$ ) and tris(hydroxymethyl)aminomethane (Tris) were obtained

from the Sigma Chemical Co. The Tris buffers were prepared by titration with perchloric acid to the desired pH. Tetramethylammonium biacetate (homoconjugate) was prepared from tetramethylammonium hydroxide (20% solution in methanol, Aldrich Chemical Co.) by potentiometric titration with glacial acetic acid. Two equivalents of acid were added for each equivalent of base, and the methanol was carefully removed on a rotary evaporator at 0.5 mm vacuum and room temperature. The resulting residue was twice taken up in AN and restripped. The final crystalline product was stored in a desiccator.

**Kinetic Method.** Two 50-mL solutions were prepared: one containing the known amount of tetraethylammonium borohydride and the other a measured amount of acetic acid and any added water. At time zero the two solutions were mixed in a bottle fitted with a plunger designed to eject a known volume of solution. Five-milliliter aliquots were ejected at recorded time intervals into bottles containing 20 mL of 0.15 M KOH to quench further reaction. For reaction solutions containing 0.1 M acetic acid (the highest concentration employed) this would result in a solution containing 20% AN and 0.10 M KOH. The amount of unreacted  $\text{BH}_4^-$  in the quenched solutions was determined by a modification in the procedure reported by Werner et al.<sup>7</sup> Within 30 min of quenching, suitable aliquots from the quench solutions (normally 0.3 mL for  $\text{BH}_4^-$  concentrations of  $2 \times 10^{-3}$  M in the original reaction mixture) were transferred to 3.0 mL of a solution containing 0.0030 M  $\text{NAD}^+$  and 0.050 M Tris buffer, adjusted to have a final pH, after addition of the quenched borohydride solution, of  $8.5 \pm 0.1$ . Under these conditions  $\text{NAD}^+$  quantitatively oxidizes  $\text{BH}_4^-$  and is itself reduced to NADH and its isomers



**Figure 1.** A typical semilogarithmic plot of  $A$  against  $t$ , illustrating the fidelity with which eq 1 describes the results. The error bars show a 5% uncertainty in  $A$ .

which have a characteristic maximum around 340 nm. The absorbances of these solutions were determined with a Gilford updated Beckman UV spectrophotometer, using as a reference the same  $\text{NAD}^+$ /Tris buffer solution to which had been added an aliquot of a quenched solution taken from the  $\text{BH}_4^-$  depleted reaction. For reactions in which the initial acid was in substantial excess over the initial  $\text{BH}_4^-$ , plots of the absorbance against time were made on semilog paper, and the best straight line was drawn through the points subjectively. From its slope the pseudo-first-order rate constant was calculated according to the following equation:<sup>8</sup>

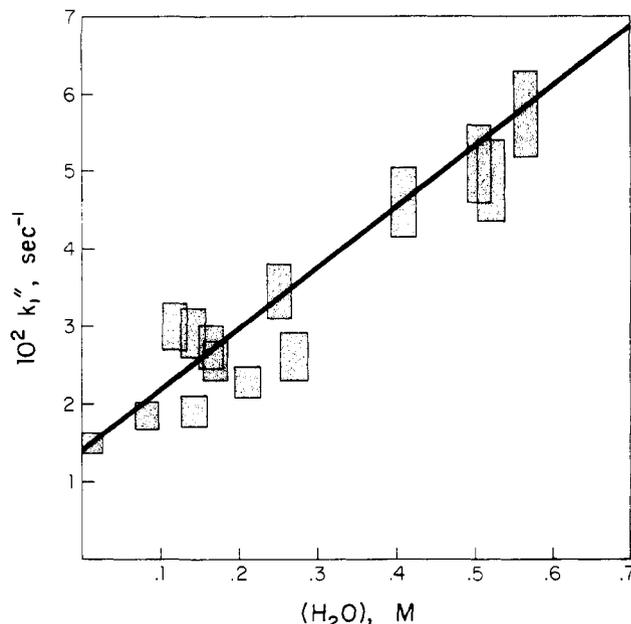
$$k_1 = \frac{2.303}{t - t_0} \log \frac{A_0 - A_\infty}{A_t - A_\infty} \quad (1)$$

Several aliquots were usually taken at the times in excess of 10 half-lives to get an average value of  $A_\infty$ . Toward the end of the reaction a sample of the reaction solution was collected for water analysis. Equation 1 describes  $A$  as a function of time with reasonable accuracy in all cases. A typical plot is shown in Figure 1. Because the reactions were generally so fast, maintenance of thermal equilibrium by use of a thermostat was not practical, and the reactions were carried out in an air-conditioned room. Initial and final temperatures were in the range of  $24 \pm 0.5^\circ\text{C}$ . Because the solutions were so dilute, there was no appreciable heat of mixing.

**Water Analysis.** The water content of the AN solutions were determined spectrophotometrically by measurement of the maximum absorbance around 1880 nm.<sup>9</sup> AN also absorbs in this region, and a calibration curve had to be obtained by preparing standard solutions. AN was dried by the method of Coetzee,<sup>5</sup> treated with  $\text{D}_2\text{O}$  to a level of 5%, redried by the same method, and, finally, shaken over molecular sieves. This sample was considered to contain no  $\text{H}_2\text{O}$ . The spectra were recorded of this sample and others, to which known amounts of water were added. A value for the base line was obtained at a point of minimum absorbance occurring about 1935 nm. This value was subtracted from the value of the maximum occurring around 1880 nm. The absorbance difference,  $A_{1880} - A_{1935}$ , designated  $A'$ , was accurately described by

$$A' = 0.110 + (0.279 \pm 0.003)(\text{H}_2\text{O}) \quad (2)$$

which was thereafter used to calculate the water content of the reaction mixtures. The amount of water found generally corresponded with the known amounts which had been added.



**Figure 2.** The effect of  $(\text{H}_2\text{O})$  on  $k_1$  at 0.1 M  $\text{CH}_3\text{COOH}$ . The solid line represents eq 3. The error bars represent a 10% uncertainty in  $k_1$  and a  $\pm 0.015$  M uncertainty in  $(\text{H}_2\text{O})$ .

## Results

Tetrahydridoborate solutions ( $2 \times 10^{-3}$  M) in AN containing 0.6 M water had half-lives of over a month. In contrast, the presence of any strong acid produced rapid hydrolysis. Thus,  $\text{BH}_4^-$  solutions ( $7 \times 10^{-4}$  M) in AN were completely hydrolyzed with half-lives of less than 5 s in the presence of  $3 \times 10^{-3}$  M  $\text{CF}_3\text{SO}_3\text{H}$ , whether or not buffered by amines. Buffered and unbuffered solutions of acetic acid gave measurable rates (typically with half-lives around 30 s). Most of the data were gathered while using an initial  $(\text{BH}_4^-)$  of  $2 \times 10^{-3}$  M. However, similar results were obtained with  $(\text{BH}_4^-)$  ranging from  $10^{-3}$  to  $10^{-1}$  M.

**Effect of Water.** With an initial acetic acid concentration fixed at 0.1 M, experiments were carried out in which the water concentration was varied from 0.007 to 0.5 M. The resulting variation in  $k_1$  is shown in Figure 2. Within its reproducibility the data can be described

$$k_1'' = 0.015 + 0.077(\text{H}_2\text{O}) \quad (3)$$

where  $k_1''$  is  $k_1$  under the conditions that  $(\text{CH}_3\text{COOH})$  is 0.1 M.

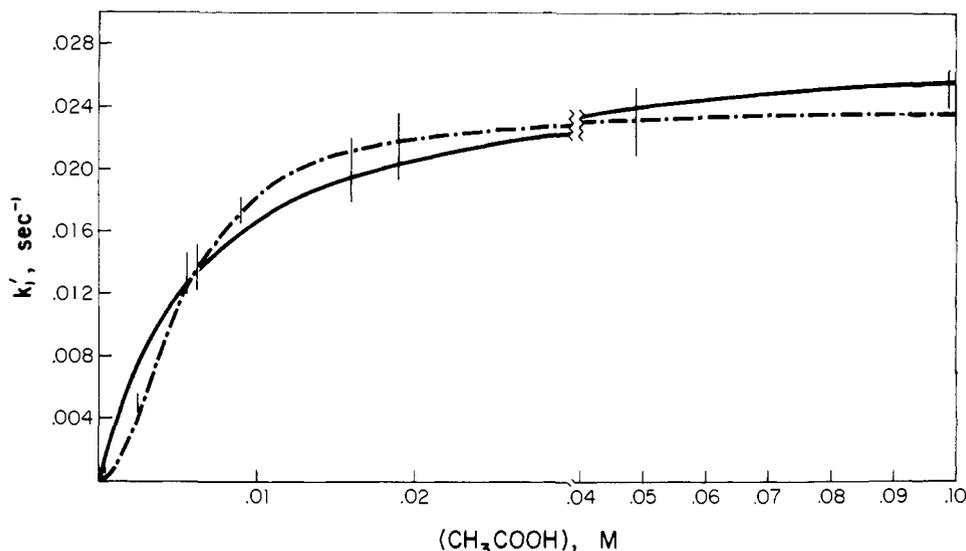
**Effect of Acetic Acid.** Thirty measurements of  $k_1$  were made at nine acetic acid concentrations ranging from  $4.8 \times 10^{-4}$  to 0.10 M. At several  $(\text{CH}_3\text{COOH})$  as many as five repetitive determinations of  $k_1$  were made. The average deviation from the mean was 10%. It was impossible to hold the water concentration constant, therefore  $(\text{H}_2\text{O})$  was measured for each run. For each  $k_1$  value a  $k_1'$  value, which would correspond to 0.135 M  $\text{H}_2\text{O}$ , was obtained using the following equation:

$$k_1' = k_1 \frac{0.015 + 0.077(0.135)}{0.015 + 0.077(\text{H}_2\text{O})} \quad (4)$$

Since the extreme variation in  $(\text{H}_2\text{O})$  was only  $\pm 0.05$  M, the  $k_1'$  value should be nearly as reliable as the  $k_1$  value. Figure 3 shows the variation in  $k_1'$  as a function of the acetic acid concentration.

Values of  $k_1$  were also measured in the presence of both acetic acid and pentamethyldiethylenetriamine, and Table I presents the results. In these runs  $k_1$  was insensitive to  $(\text{H}_2\text{O})$ . At 0.5 M acetic acid, addition of the amine increased  $k_1$ .

**Catalysis by Biacetate.** The hydrolysis of 0.3 M  $\text{BH}_4^-$  was



**Figure 3.** The effect of  $(\text{CH}_3\text{COOH})$  on  $k_1'$ . The error bars represent the uncertainty in the experimental values of  $k_1'$ , which is 10%, except at 0.09 and 0.099 M  $\text{CH}_3\text{COOH}$ , where multiple runs reduced the uncertainty. The solid line represents eq 16. The dotted line represents eq 17. For each equation the best parameters were used.

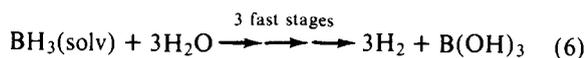
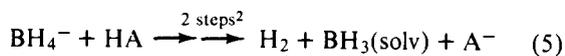
also monitored in an acetonitrile solution containing 0.18 M  $\text{H}_2\text{O}$  and 0.1 M tetramethylammonium biacetate. The plot of  $\log A$  against time was nonlinear, its slope decreasing steadily with time. The initial  $k_1'$  was only  $2.12 \times 10^{-3}$ . This could be attributed to the free acetic acid present in equilibrium with the biacetate. The biacetate itself appears to be inactive as a catalyst.

**High  $\text{BH}_4^-$  Concentrations.** In these experiments the  $(\text{BH}_4^-)$  was monitored in solutions initially containing about 0.3 M of  $\text{BH}_4^-$ , 0.4 M of  $\text{CH}_3\text{COOH}$ , and about 0.15 M of  $\text{H}_2\text{O}$ . The initial rates were very high, but plots of  $\log A$  against time were strongly nonlinear and reached almost constant, nonzero values of  $A$  after about a hour. A typical result is shown in Figure 4. It can be understood in the context of the mechanism which is proposed in the discussion section if the biacetate ion is assumed to be catalytically inactive.

**$^{11}\text{B}$  NMR Studies.** The  $^{11}\text{B}$  resonance of 0.1 M  $\text{Et}_4\text{N}^+\text{BH}_4^-$  solutions in AN containing 0.5 M  $\text{D}_2\text{O}$  were examined before and after addition of 15, 30, 60, and 100% of the acetic acid required to decompose the  $\text{BH}_4^-$ . The  $^{11}\text{B}$  spectra of the partially hydrolyzed solution showed only the characteristic five lines of the parent ion. No partially deuterated material and no other boron hydride species could be detected. Similar experiments with methanesulfonic acid yielded similar results.

## Discussion

The hydrolysis of  $\text{BH}_4^-$  takes place in four stages:



In water it has been shown that the first, to give solvated  $\text{BH}_3$ , is almost completely rate determining,<sup>10,11</sup> although low concentrations of partially hydrolyzed intermediates can be detected. No intermediates have been detected in  $\text{Me}_2\text{SO}$ ,<sup>4</sup> and the  $^{11}\text{B}$  NMR results described above imply that this is also true in AN. The following discussion, therefore, pertains entirely to the first stage. The  $\text{pK}_a$  of acetic acid in AN is 22.3.<sup>12</sup> Considering that borohydride preparations are always contaminated with basic impurities, and the reaction produces base, there is insufficient  $\text{H}^+$  to contribute measurably to the rate, even if the reaction with  $\text{BH}_4^-$  were diffusion controlled.

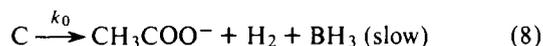
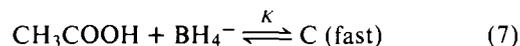
**Table I.** Rates as a Function of Acetic Acid and Pentamethyldiethylenetriamine Concentrations

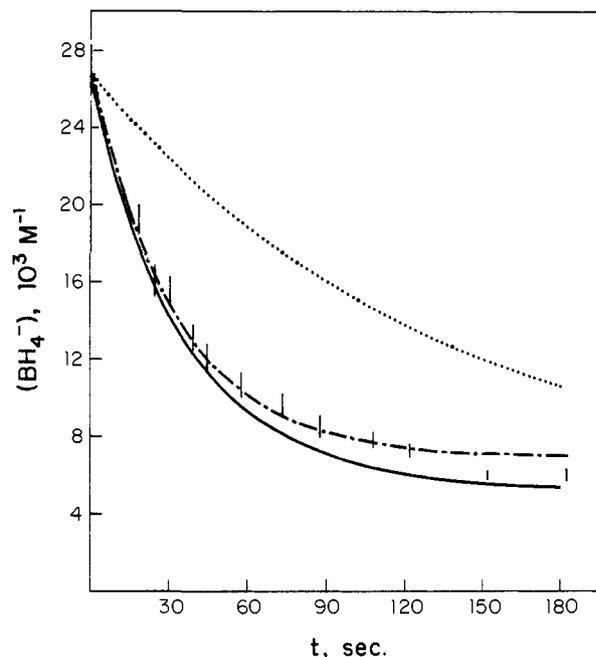
$(\text{CH}_3\text{COOH}),$ M	(PMDETA), M	$k_1 \times 10^2,$ $\text{s}^{-1}$
0.01		1.75 <sup>a</sup>
0.01	0.015	1.31
0.01	0.054	0.83
0.01	0.115	0.77 <sup>a</sup>
0.02		2.15
0.02	0.115	1.90
0.04		2.30 <sup>b</sup>
0.04	0.056	5.51
0.04	0.115	3.33 <sup>a</sup>

<sup>a</sup> Average value. <sup>b</sup> Extrapolated value.

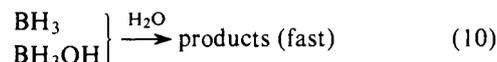
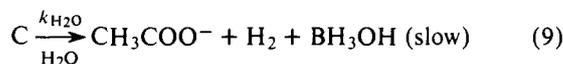
In fact, no sign of its participation appears in the rate law, and we have not considered it further. Since no measurable reaction occurs in the absence of a stronger acid, even when 0.5 M water is present, acid catalysis by water must also be insignificant, presumably because water is such a weak acid in AN. Because the conjugate acid of PMDETA is probably internally hydrogen bonded, its role as an acid catalyst is unlikely to be important either. Acetic acid is regarded as the only significant acid catalyst in all of these reactions.

Figure 3 strongly suggests the essentially complete complexing of  $\text{BH}_4^-$  by acetic acid at the higher acid concentrations. Figure 2 indicates that the disappearance of  $\text{BH}_4^-$  (and/or any complex of it) has both a water promoted and an unpromoted path. In the amine buffered solutions the rate was actually increased by the addition of amine at the higher acid concentrations. The amine would be expected to decrease the concentration of any acetic acid- $\text{BH}_4^-$  complex by competing with  $\text{BH}_4^-$  for complexing acetic acid. Since, at high acid concentrations, it actually increased the observed rate, it most probably functioned as a nucleophile, which is probably the role of the water as well. The mechanism below qualitatively fits the results and will be shown to fit quantitatively as well (C represents the  $\text{BH}_4^-$ - $\text{CH}_3\text{COOH}$  complex):





**Figure 4.** The consumption of  $\text{BH}_4^-$  in a solution originally containing 0.269 M  $\text{BH}_4^-$ , 0.434 M  $\text{CH}_3\text{COOH}$ , and 0.185 M  $\text{H}_2\text{O}$ . The solid line is the prediction of eq 12 and 20, while the dotted line is the prediction of eq 12 and 21. The dot-dash line is the prediction of eq 12 and 20 with the initial  $(\text{CH}_3\text{COOH})$  arbitrarily adjusted to 0.400 M. In each case the parameters were those obtained from the low-concentration experiments.



The rate law given by this mechanism is shown in eq 11–16 under the condition that  $(\text{CH}_3\text{COOH})$  and  $(\text{H}_2\text{O})$  are always in large excess over  $(\text{BH}_4^-)_t$ , which is the analytically determined concentration of  $\text{BH}_4^-$  at any time,  $t$ :

$$\frac{-d(\text{BH}_4^-)_t}{dt} = k_1(\text{BH}_4^-)_t \quad (11)$$

$$\frac{-d(\text{BH}_4^-)_t}{dt} = [k_0 + k_{\text{H}_2\text{O}}(\text{H}_2\text{O})](\text{C}) \quad (12)$$

$$(\text{BH}_4^-)_t = (\text{BH}_4^-) + (\text{C}) \quad (13)$$

$$(\text{C}) = K(\text{CH}_3\text{COOH})[(\text{BH}_4^-)_t - (\text{C})] \quad (14)$$

$$(\text{C}) = \frac{K(\text{CH}_3\text{COOH})(\text{BH}_4^-)_t}{1 + K(\text{CH}_3\text{COOH})} \quad (15)$$

$$k_1 = [k_0 + k_{\text{H}_2\text{O}}(\text{H}_2\text{O})] \left[ \frac{K(\text{CH}_3\text{COOH})}{1 + K(\text{CH}_3\text{COOH})} \right] \quad (16)$$

For convenience  $[k_0 + k_{\text{H}_2\text{O}}(\text{H}_2\text{O})]$  was defined as  $k_s$  when  $(\text{H}_2\text{O})$  was 0.135 M. Values of  $K$  and  $k_s$  were obtained which minimize the sum of the squares of the differences between the experimental values of  $k_1'$  and the values of  $k_1$  given by eq 16.<sup>13</sup> The values are  $1.6 \pm 0.3 \times 10^2 \text{ M}^{-1}$  and  $2.72 \pm 0.14 \times 10^{-2} \text{ s}^{-1}$ , respectively. The uncertainties are probable errors. The discrepancy between this value of  $k_s$  and the value of  $[k_0 + k_{\text{H}_2\text{O}}(\text{H}_2\text{O})]$  for 0.135 M  $\text{H}_2\text{O}$  derived from the measurements at constant  $(\text{CH}_3\text{COOH})$ <sup>14</sup> is well within the sum of the two uncertainties, as it should be, since a substantial amount of the same data was used in both determinations. In subsequent calculations the best values of  $k_0$  and  $k_{\text{H}_2\text{O}}$  are individually required. The values accepted were  $0.0168 \text{ s}^{-1}$  and  $0.0773 \text{ M}^{-1} \text{ s}^{-1}$ , respectively, thus assuming that the discrepancy between

the two values of  $k_s$  lies in  $k_0$ . Figure 3 shows the fit of eq 16 to the experimental points using the best values of the parameters.

A better fit of the data can be given by

$$k_1' = \frac{k_s'K'(\text{CH}_3\text{COOH})^2}{1 + K'(\text{CH}_3\text{COOH})^2} \quad (17)$$

as illustrated in the same Figure. A similar mechanism is required by this equation, except that the complex must involve two molecules of acetic acid with one of  $\text{BH}_4^-$ . Here  $K'$  represents the overall equilibrium for the postulated 2:1 acetic acid– $\text{BH}_4^-$  complex, and  $k_s'$  is the first-order rate constant for the hydrolysis of the complex when  $(\text{H}_2\text{O})$  is 0.135 M. Complexes formed from an anion and two molecules of a proton donor have been reported in An with high formation constants.<sup>15–17</sup> The data were similarly analyzed according to eq 17. Values of  $2.36 \pm 0.05 \times 10^{-2} \text{ s}^{-1}$  and  $3.5 \pm 0.4 \times 10^4 \text{ M}^{-2}$  were generated for  $k_s'$  and  $K'$ , respectively.

To distinguish between the two possible formulations of the complex, experiments were conducted at nearly comparable  $(\text{BH}_4^-)$  and  $(\text{CH}_3\text{COOH})$ , approximately 0.3 and 0.4 M, respectively. Under these conditions the reaction would initially be about twice as fast if the complex required one molecule of acetic acid rather than two, since there is enough acetic acid to convert almost all of the  $\text{BH}_4^-$  to binary complex, but only half of it to the ternary complex. Further, each mole of  $\text{BH}_4^-$  that reacts removes two moles of acetic acid from the system (eq 23): one is converted to acetate ion; the other is almost completely inactivated through the formation of the biacetate.<sup>12</sup> Thus, if a ternary complex is required, the rate would be still further retarded, from the very beginning, by an increasing shortage of acetic acid. The problem is much less acute if only a binary complex is required. These considerations can be quantified as follows. Equations 11, 12, and 13 are still valid, but, since acetic acid is no longer in large excess,  $(\text{CH}_3\text{COOH})_t$ , the analytical concentration of acetic acid at time  $t$ , is given by eq 18 if C is binary, by eq 19 if it is ternary. Equation 20 then gives  $(\text{C})_t$  if the complex is binary; eq 21 if the complex is ternary. If  $\Delta t$  is made small enough,  $(\text{BH}_4^-)_{t+\Delta t}$  is given by eq 22; eq 23 and 24 give  $(\text{HA})_{t+\Delta t}$  and

$(\text{H}_2\text{O})_{t+\Delta t}$ :

$$(\text{CH}_3\text{COOH})_t = (\text{CH}_3\text{COOH}) + (\text{C})_t \quad (18)$$

$$(\text{CH}_3\text{COOH})_t = (\text{CH}_3\text{COOH}) + 2(\text{C})_t \quad (19)$$

$$K = \frac{(\text{C})_t}{[(\text{CH}_3\text{COOH})_t - (\text{C})_t][(\text{BH}_4^-)_t - (\text{C})_t]} \quad (20)$$

$$K' = \frac{(\text{C})_t}{[(\text{CH}_3\text{COOH})_t - 2(\text{C})_t]^2[(\text{BH}_4^-)_t - (\text{C})_t]} \quad (21)$$

$$(\text{BH}_4^-)_{t+\Delta t} = (\text{BH}_4^-)_t - \{[k_0 + k_{\text{H}_2\text{O}}(\text{H}_2\text{O})](\text{C})_t\} \Delta t \quad (22)$$

$$(\text{CH}_3\text{COOH})_{t+\Delta t} = (\text{CH}_3\text{COOH})_t - 2[(\text{BH}_4^-)_t - (\text{BH}_4^-)_{t+\Delta t}] \quad (23)$$

$$(\text{H}_2\text{O})_{t+\Delta t} = (\text{H}_2\text{O})_t - 3[(\text{BH}_4^-)_t - (\text{BH}_4^-)_{t+\Delta t}] \quad (24)$$

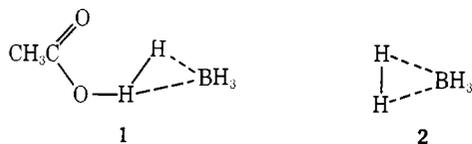
Assuming the binary complex, it is possible to start with the initial concentration of  $\text{BH}_4^-$ ,  $\text{CH}_3\text{COOH}$ , and  $\text{H}_2\text{O}$ , and to use eq 20, 22, 23, and 24 to calculate, by small increments,  $(\text{BH}_4^-)_t$  as a function of  $t$ , for the whole period of the reaction. The  $\Delta t$  used was 2 s. This corresponds to no more than 5% reaction. Best values for all the required constants are available from the experiments with low  $(\text{BH}_4^-)$ . Using eq 21–24,<sup>18</sup> the same procedure may be employed assuming a ternary complex. These calculations have been carried out using a CDC 6600 digital computer, and the calculated curves are shown, along with the experimental values, in Figure 4. It is clear that the

binary complex allows an acceptable prediction of the  $(\text{BH}_4^-)$ , to be made, while the ternary complex does not. Figure 4 also shows that a perfect fit could be obtained by postulating a slightly lower  $(\text{CH}_3\text{CO}_2\text{H})$  than that to which the reaction mixture was made up. The  $(\text{CH}_3\text{CO}_2\text{H})$  could easily have been slightly reduced by the basic impurities with which  $\text{BH}_4^-$  preparations are commonly contaminated. These would not have been a significant factor in other experiments because of the low  $(\text{BH}_4^-)$ .

The preceding analysis neglects dissociation of the biacetate and also solution nonideality that may result from the high concentrations used. Using the known<sup>12</sup> constant for biacetate formation, the former effect can be shown to be small, and this has been experimentally verified. High concentrations of water have been shown to give results in accord with eq 14. At the 0.1 M acetic acid level the results have been shown to be independent of the  $(\text{C}_2\text{H}_5)_4\text{N}^+\text{BH}_4^-$  concentration. These observations suggest that the neglected effects are not large.

The mechanism in AN presents some interesting contrasts to those in  $\text{Me}_2\text{SO}$  and in water. The catalytic coefficient for  $\text{H}^+(\text{solv})$  in AN is immeasurable because any acid which could provide  $\text{H}^+(\text{solv})$  in reasonable concentration in AN appears to give immeasurably fast rates. Nevertheless, from the circumstances it appears that  $k_{\text{H}^+}$  would be much larger than in  $\text{Me}_2\text{SO}$ . This shows, as expected, that the proton-binding ability of  $\text{Me}_2\text{SO}$ , as well as its inability to furnish a proton, is responsible for the small catalytic coefficient for  $\text{H}^+$  in that solvent.<sup>4</sup> The acetic acid homoconjugate in AN, which has a structural resemblance to  $\text{H}^+(\text{solv})$  in  $\text{Me}_2\text{SO}$ ,<sup>19</sup> shows no measurable catalytic activity at all.

The absence of deuterium uptake by unreacted  $\text{BH}_4^-$  in AN containing  $\text{D}_2\text{O}$  and  $\text{CH}_3\text{CO}_2\text{D}$  requires that the acetate ion remain firmly bonded to the proton which it donated to  $\text{BH}_4^-$  until the complex decomposes to give  $\text{CH}_3\text{COO}^-$ ,  $\text{H}_2$  or  $\text{HD}$ , and  $\text{BH}_3$  or  $\text{BH}_3\text{OH}_2$ . The complex probably has structure **1**.



It is analogous to structure **2**, which has been shown to be most stable for  $\text{BH}_5$ ,<sup>20-22</sup> but distorted by strong interactions between the acetate ion and one of the protons of the  $\text{H}_2$  unit. Its existence provides support for the postulate that  $\text{BH}_5$  is an intermediate in the aqueous solution hydrolysis because substances which can act as hydrogen bond acceptors can usually also act as Bronsted bases under suitable conditions.<sup>23</sup> Nevertheless, there is a considerable contrast between the present result and that for the water acting as an acid in aqueous solution. In that case, after  $\text{H}_2\text{O}$  attaches a proton to  $\text{BH}_4^-$ ,  $\text{OH}^-$  diffuses away, leaving **2**.<sup>2</sup> The difference may be due to the ready availability of hydrogen bond donor sites in aqueous solution. In AN the absence of competitive hydrogen bond

donors may keep the  $\text{CH}_3\text{COO}^-$  firmly fixed to a single site on the  $\text{BH}_5$ , as in **1**. Another difference is that **2**, and its cyano analogue  $\text{BH}_4\text{CN}$ , appear to have very high rates for spontaneous evolution of  $\text{H}_2$  and without the intervention of nucleophilic reagents.<sup>20,24</sup> The rate constant for spontaneous decomposition of **1**,  $k_0$ , is modest, and nucleophilic expulsion of  $\text{H}_2$  is evident. These differences reasonably follow from the structural differences between **1** and **2**. The  $\text{H}_2$  unit in the latter much more nearly resembles the separated  $\text{H}_2$  molecule.

**1** represents one of the few examples of a hydrogen bond in which the acceptor has neither a nonbonded pair of electrons nor a  $\pi$  bonded pair. Its formation constant is similar to that for  $\text{CH}_3\text{COOH}$  with  $\text{Cl}^-$  in acetonitrile ( $K_f$  is  $1.7 \times 10^2$ ).<sup>15</sup> Infrared evidence has been reported for a similar complex involving dimethylaminoborane and phenols in chloroform,<sup>25</sup> and cyclopropane has also been suggested as a hydrogen bond acceptor.<sup>26</sup> The observation of the acetic acid- $\text{BH}_4^-$  complex is greatly facilitated by the fact that AN is a very weak competitor as a hydrogen bond acceptor.

## References and Notes

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- (13) Library Program "FUTURE SPSS" of the University of Minnesota Numerical Analytical Center was used in a CDC 6600 computer.
- (14) Since  $\text{BH}_4^-$  is only 94% saturated at 0.1 M acetic acid, the  $k_s$  value derived from the parameters in eq 2 is  $2.70 \times 10^{-2}$ .
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- (18) Equation 19 is a cubic equation. To find the roots of  $C$ , they were first approximated by trial and error, then the lowest real value was refined by Newton's method. Equation 18, however, was a simple quadratic equation and was solved analytically.
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