

extremely grateful to C. H. Bushweller for helpful comments and suggestions concerning the spectral simulation studies. Support for the 220-MHz NMR studies was provided by a grant from the Alfred P. Sloan Foundation administered by the Southern Regional Education Board.

Registry No.  $\text{B}_4\text{H}_8\text{PF}_2\text{N}(\text{CH}_3)_2$ , 24778-60-7.

### References and Notes

- (1) Part 18 in the series "Spectra and Structure of Phosphorus-Boron Compounds". For Part 17 see J. R. Durig, P. J. Cooper, E. J. Stampf, and J. D. Odom, *Spectrochim. Acta, Part A*, **34**, 633 (1978).
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- (30) If part of the framework bonding involving  $\text{B}_1$  is disturbed, rehybridization of  $\text{B}_3$  and closure of the bonding to  $\text{B}_1$  could cause interchange of the isomers. This mechanism is somewhat analogous to what we have referred to as the "ring flip" mechanism; however, rehybridization of only one boron atom is necessary. This rehybridization could be much more facile once the framework electronic structure is perturbed.

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## Hydrolysis Mechanism of $\text{BH}_4^-$ in Moist Acetonitrile. 3. Kinetic Isotope Effects

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The present work and a concurrent paper<sup>1</sup> show that, in the presence of acetic acid,  $\text{BH}_4^-$  in acetonitrile is rapidly converted to  $\text{BH}_3\text{OCOCH}_3^-$  and that previous kinetic studies of the hydrolysis of  $\text{BH}_4^-$  in such solutions<sup>2</sup> actually referred to the hydrolysis of  $\text{BH}_3\text{OCOCH}_3^-$ . As previously shown, the substrate (now shown to be  $\text{BH}_3\text{OCOCH}_3^-$ ) complexes with acetic acid, with a complexing constant of about 160. That complex hydrolyzes by spontaneous and water-catalyzed paths. The present paper shows that the latter reaction is *accelerated* 15–40% by the substitution of D for H on boron. The rate is reduced, by a factor of  $\sim 1.75$ , by replacing all the hydroxylic hydrogen with deuterium. These results are consistent with  $\text{BH}_3\text{OC}(\text{CH}_3)\text{O}\cdot\text{HOCOCH}_3$  (**2**) as the acetic acid–substrate complex. The displacement of the incipient biacetate ion by water is rate determining in this process. Isotopic substitution at either position reduces the rate of the spontaneous process. Its mechanism is uncertain.

A kinetic study of the acidolysis of tetrahydroborate ion ("borohydride") in moist acetonitrile<sup>2</sup> gave evidence that the reaction proceeds via a mechanism involving the accumulation of an intermediate complex. The reversible formation of a complex, **1**, between borohydride ion and acetic acid was proposed to account for this kinetic requirement. Subsequent NMR studies of intermediates and of isotopic exchange in the reactants in the acidolysis reaction<sup>1</sup> confirm that the intermediate proposed by Modler and Kreevoy is formed reversibly in the course of the reaction but indicate that it does not accumulate. Instead, the rate-determining stage of the reaction involves a second intermediate, trihydroacetoxyborate ion,  $\text{CH}_3\text{COOBH}_3^-$ , which plays the role assigned to  $\text{BH}_4^-$  by Modler and Kreevoy. The place of **1** is taken by the H-bonded acetic acid complex of  $\text{CH}_3\text{COOBH}_3^-$ , **2**. With these substitutions the rate law of Modler and Kreevoy<sup>2</sup> is still applicable.

The present kinetic study, by examining the effect of deuterium substitution in the reactants, leads to additional insight into the reaction mechanism. Through the use of a borohydride salt more readily obtainable in pure form, the kinetic data of Modler and Kreevoy<sup>2</sup> are refined to give more precise rate constants. The water-promoted pathway is shown to involve nucleophilic attack by water on the complex **2**.

### Experimental Section

**Materials.** Commercial acetonitrile, 99% pure or better, was stirred 24 h over molecular sieves, decanted, stirred an additional 24 h over calcium hydride, and distilled from calcium hydride through a short fractionating column. The samples used in the kinetic experiments contained water concentrations ranging from less than 0.01 to 0.025 M. Sodium tetrahydroborate, both 98% powder and stable aqueous solution (4.4 M  $\text{NaBH}_4$  in 14 M NaOH), sodium tetradeuterioborate, cesium acetate (ultrapure), and bis(triphenylphosphin)iminium chloride ( $(\text{Ph}_3\text{P})_2\text{N}^+\text{Cl}^-$ ) were obtained from the Alfa Division of the Ventron

Corp. and used as received. Acids and bases were AR grade. Deuterium oxide was obtained from Aldrich Chemical Co. and was stated to contain 99.7 atom % D. Acetonitrile- $d_3$  was obtained from Merck and Co. and was stated to contain 99 atom % D. Acetic acid- $d_1$  was prepared by the method of Roberts, Regan, and Allen<sup>3</sup> from glacial acetic acid and  $D_2O$ . Water used in the kinetic experiments was deionized and then distilled in glass through a short fractionating column.

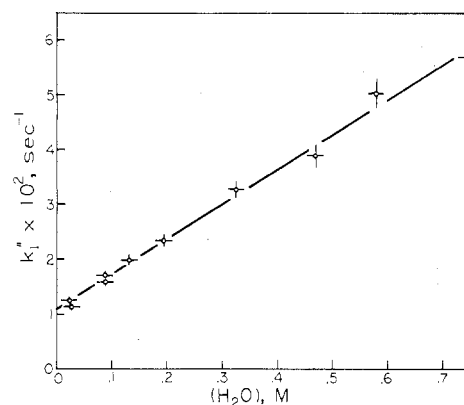
**1-Benzyl-3-carbamylpyridinium Chloride (Benzylnicotinamide Chloride, BNA<sup>+</sup>Cl<sup>-</sup>).** This material was prepared by the method of Büchi et al.<sup>4</sup> yield 75.5 g, 60.9%; UV spectrum in water  $\lambda_{max}$  263 nm,  $\epsilon$  4490 (lit.<sup>6</sup>  $\lambda_{max}$  265 nm,  $\epsilon$  4400); mp 232–233.5 °C (uncor) (lit. mp 236 °C,<sup>7</sup> 258.5 °C<sup>5</sup>). This product was used without further purification.

**Bis(triphenylphosphin)iminium<sup>7</sup> Tetrahydroborate ((Ph<sub>3</sub>P)<sub>2</sub>N<sup>+</sup>BH<sub>4</sub><sup>-</sup>).** To a solution of 5.76 g, 0.0101 mol, of (Ph<sub>3</sub>P)<sub>2</sub>N<sup>+</sup>Cl<sup>-</sup> in 800 mL of glass-distilled water at 62 °C was added, from a pipet during 30 s, 2.50 mL,  $\geq 0.0101$  mol, of 4.4 M NaBH<sub>4</sub> in 14 M aqueous NaOH with continuous magnetic stirring. The instantaneously formed precipitate redissolved and then quickly recrystallized. The stirred suspension was cooled as rapidly as possible in an ice bath to 20 °C, filtered through a coarse sintered-glass funnel, washed four times with a total of 50 mL of ice-cold 0.25 M NH<sub>4</sub>OH, and dried in vacuo for 6 days under continuous mechanical pumping; yield 4.90 g, 0.00885 mol, 87.6%. The IR spectrum in Nujol mull shows B–H stretching frequencies at 2125, 2215, and 2265  $cm^{-1}$  (lit.<sup>9</sup> 2130, 2220, 2280  $cm^{-1}$ ). Also present are slight traces of water (absorption band 3440–3520  $cm^{-1}$ ) and triphenylphosphine oxide<sup>10</sup> (absorption band at 1188  $cm^{-1}$ , checked against an authentic specimen). Further attempts at drying were of no avail. Attempts at recrystallization always resulted in an increase in the triphenylphosphine oxide absorption bands. Analysis with BNA by the method used in the measurement of rates and calibrated against standardized<sup>11</sup> aqueous alkaline NaBH<sub>4</sub> indicated the presence of 95% of theoretical BH<sub>4</sub><sup>-</sup>. Elemental analysis and the spectra cited above suggest that the other 5% consists largely of water, triphenylphosphine oxide, and bis(triphenylphosphin)iminium borate.

**Bis(triphenylphosphin)iminium<sup>7</sup> Tetra-deuterioborate ((Ph<sub>3</sub>P)<sub>2</sub>N<sup>+</sup>BD<sub>4</sub><sup>-</sup>).** The procedure used for (Ph<sub>3</sub>P)<sub>2</sub>N<sup>+</sup>BH<sub>4</sub><sup>-</sup> was followed by using 2.50 mL, 0.00813 mol, of 3.25 M NaBD<sub>4</sub> in 12 M NaOH, starting with NaBD<sub>4</sub> powder; yield 3.48 g, 0.00624 mol, 76.6%. The IR spectrum shows moderately strong, broad B–D stretching bands with peaks at 1620 and 1685  $cm^{-1}$ . Only a trace of the B–H band at 2220  $cm^{-1}$  appeared, indicating isotopic purity of 95% or better. No water was detectable in the IR spectrum, and there was only a trace of triphenylphosphine oxide (1188  $cm^{-1}$ ). Anal. Calcd for C<sub>36</sub>H<sub>30</sub>D<sub>4</sub>BNP<sub>2</sub>: C, 77.57; H (+D), 6.87; N, 2.51; P, 11.11. Found C, 77.31; H (+D), 6.59; N, 2.29; P, 11.29.

**Kinetic Methods.** A modification of the procedure of Modler and Kreevoy<sup>2</sup> was used. Two solutions were prepared in acetonitrile, one containing 0.0090 M (Ph<sub>3</sub>P)<sub>2</sub>N<sup>+</sup>BH<sub>4</sub><sup>-</sup> or (Ph<sub>3</sub>P)<sub>2</sub>N<sup>+</sup>BD<sub>4</sub><sup>-</sup> and the other containing 0.20 M acetic acid or acetic acid- $d_1$  and varying amounts of water or D<sub>2</sub>O. At time zero 50-mL volumes of each solution were mixed in a reaction bottle fitted with a syringe pump designed to eject aliquots of a predetermined size. Aliquots were ejected at timed intervals into bottles containing 20 mL of aqueous 0.15 M NaOH quench solution. Five-milliliter aliquots were intended, but rapid evolution of hydrogen made reproducibility of aliquot volume impossible. Consequently the quench bottles were weighed before and after the addition of the aliquots to determine aliquot weights. Within 1 h a 0.50-mL aliquot of each quenched solution was added to a second bottle containing 5 mL of 0.020 M BNA in aqueous 0.050 M NaHCO<sub>3</sub> to give a final carbonate–bicarbonate buffered solution of pH 9.38  $\pm$  0.10. The unreacted reducing agent in the quenched solutions converted BNA<sup>+</sup> to (BNA)H, which was measured spectrophotometrically at 358 nm with a Beckman Model DU spectrophotometer with a tungsten lamp. Reactions were carried out without further temperature control in a room maintained at 25  $\pm$  1 °C. Absorbances were corrected for variation in the original aliquot size and the data used to calculate pseudo-first-order rate constants as reported previously.<sup>2</sup>

**Water Analysis.** The previously reported method of Modler and Kreevoy,<sup>2</sup> using the H<sub>2</sub>O absorption at 1880 nm measured with a Beckman Model DK-2 spectrophotometer, for determination of low concentrations of water in acetonitrile solutions gives very good results in the absence of other substances.<sup>12</sup> Acetic acid interferes, however,



**Figure 1.** Plot of observed rate constants,  $k_1''$ , vs. water concentration for reaction of 0.0045 M BH<sub>4</sub><sup>-</sup> with 0.10 M CH<sub>3</sub>COOH in moist acetonitrile. Error bars indicate estimated uncertainties in measurements.

perhaps by association with water, and the method is not applicable to D<sub>2</sub>O or any of its mixtures with H<sub>2</sub>O. A corrected formula for H<sub>2</sub>O determination in the presence of 0.1 M HOAc was developed by analysis of a series of acetonitrile solutions of increasing water content up to about 0.75 M followed by addition of glacial acetic acid sufficient to give an acetic acid concentration of 0.100 M. Redetermination of solution absorbances after the addition of acetic acid led to eq 1, valid only for acetonitrile solutions containing 0.10 M

$$[H_2O] = (A' - 0.105)/(0.269 \pm 0.003) \quad (1)$$

$$A' = A_{1880 \text{ nm}} - A_{1938 \text{ nm}} \quad (1\text{-mm light path})$$

acetic acid. In those kinetic experiments in which CH<sub>3</sub>COOH was used, water concentration was calculated by eq 1 with data obtained from a sample of residual reaction mixture after the B–H compounds were exhausted.

For those experiments in which CH<sub>3</sub>COOD was used, with or without added D<sub>2</sub>O, we know of no direct method for determining water content, since some HOD and perhaps H<sub>2</sub>O should be present in addition to D<sub>2</sub>O. For these experiments an estimate of the water content was made by one of two methods. Usually, two experiments were performed on the same day under conditions as nearly identical as possible except for the isotopic content of the acetic acid and any added water. The water content of the reaction mixture containing CH<sub>3</sub>COOH was measured, and the other was assumed to be the same. In experiments in which this pairing of reactions was not done, the water content was estimated to be the sum of the concentration of added D<sub>2</sub>O, the known very low water content of the solvent, and an average value for adventitious water as determined for those experiments in which it could be measured. We believe that any error introduced by inaccurate estimates of water content is smaller than other unavoidable errors and, hence, does not significantly reduce the reliability of results.

## Results

**Purity of Reaction Solvents.** Early results, with ordinary deionized water both in the reaction mixture and as the final rinse in cleaning reaction vessels, gave one observed rate constant 60% larger than would be predicted from Figure 1 and another too large to be measurable at all by our method. Subsequently only glass-distilled water was used in the reaction mixtures and all glassware, after thorough cleaning, was given a final rinse with glass-distilled solvent. No further aberrant values of rate constants were observed, and scatter was noticeably reduced in individual experiments.

**Nature of the Quenched Reducing Agent.** It was observed that quenched aliquots of the reaction mixture in the kinetic experiments react visibly much faster with BNA<sup>+</sup> than does BH<sub>4</sub><sup>-</sup> under the same conditions. The reaction of BH<sub>4</sub><sup>-</sup> with BNA<sup>+</sup> to give (BNA)H was found to have a pseudo-first-order rate constant of 0.040 s<sup>-1</sup> at 25 °C. Under similar conditions quenched aliquots from the reaction mixture in acidolysis of BH<sub>4</sub><sup>-</sup> by acetic acid in acetonitrile reacted too fast to be

Table I. Calculated Rate Constants

series	reactants	no. of expts	$k_0, \text{s}^{-1} \times 10^2$ <sup>a</sup>	$k_{\text{H}_2\text{O}}, \text{s}^{-1} \times 10^2$ <sup>a</sup>	corrln coeff
I	$\text{BH}_4^- + \text{CH}_3\text{COOH}/\text{H}_2\text{O}$	10	$1.10 \pm 0.06$	$6.34 \pm 0.18$	0.997
II	$\text{BD}_4^- + \text{CH}_3\text{COOH}/\text{H}_2\text{O}$	12	$0.91 \pm 0.22$	$9.10 \pm 0.66$	0.975
III	$\text{BH}_4^- + \text{CH}_3\text{COOD}/\text{D}_2\text{O}$	5	$0.92 \pm 0.06$	$4.08 \pm 0.17$	0.996
IV	$\text{BD}_4^- + \text{CH}_3\text{COOD}/\text{D}_2\text{O}$	7	$0.85 \pm 0.15$	$4.65 \pm 0.48$	0.977

<sup>a</sup> The standard error of estimate,  $S_y$ , is used to provide the tabulated uncertainties.

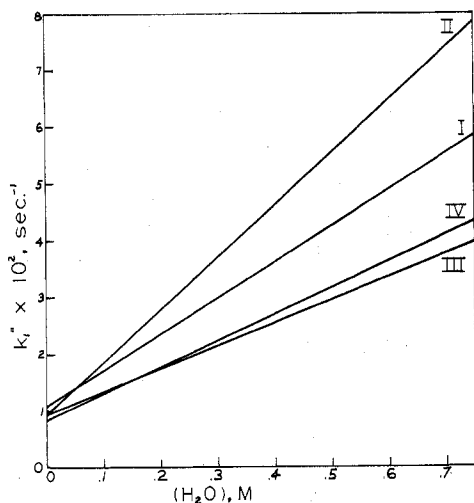


Figure 2. Plots of observed rate constants vs. water concentration for reactions of borohydride ion with acetic acid in moist acetonitrile in four reaction series of different hydrogen isotopic composition. Roman numerals relate to reactants as tabulated in Table I.

measured by our method, at least 20 times as fast as  $\text{BH}_4^-$  and with a half-life of less than 1 s. No evidence was found for the presence of any  $\text{BH}_4^-$  in those quenched aliquots.

In the hydrolysis of  $\text{BH}_4^-$  by moist, acidic, acetonitrile, extrapolation to zero time of a plot of  $\log A$  vs. time for a typical kinetic experiment indicates that the reducing power of the quenched aliquots corresponds, very roughly, to three B-H bonds per initial mole of  $\text{BH}_4^-$ . These results, together with the spectroscopic results,<sup>1</sup> show that the principal B-H compound in the quenched solutions is  $\text{BH}_3\text{OH}^-$ .

**Kinetics of Borohydride Acidolysis.** A typical series of kinetic experiments is presented graphically in Figure 1. The linear least-squares regression program in a Texas Instruments Model SR-56 programmable hand calculator was used to fit a straight line to the data points. Four series of kinetic experiments were carried out by employing the four possible combinations of ordinary hydrogen and deuterium in the reagents. For each series the  $k_1''$  values<sup>13</sup> were fitted to eq 2. These results are presented graphically in Figure 2 and

$$k_1'' = k_1(\text{obsd}) = k_0 + k_{\text{H}_2\text{O}}[\text{H}_2\text{O}] \quad (2)$$

the parameters  $k_0$  and  $k_{\text{H}_2\text{O}}$ , along with the correlation coefficients, are given in Table I.

It is difficult or impossible without a very large number of kinetic experiments to make a reliable assessment of the uncertainties in the calculated values of  $k_0$  and  $k_{\text{H}_2\text{O}}$ . The isotope effects in Tables II and III are quotients of two rate constants, and the tabulated uncertainties in these quotients are calculated by a standard method for calculating most probable error in quotients of numbers having indeterminate errors.<sup>14</sup> This assumption of randomness in the uncertainties in rate constants leads to very large uncertainties in isotope effects, leading in turn to some uncertainty in the direction of the isotope effect in  $k_0$ . Except for water concentration, the reaction conditions and the procedure for analysis of results are nearly identical for all of the kinetic experiments. It seems reasonable to assume, therefore, that errors in determination

Table II. Isotope Effects on  $k_0$ 

rate const	reactants		$k_0^{\text{H}}/k_0^{\text{D}}$ <sup>b</sup>
	$\text{BL}_4^-$	$\text{CH}_3\text{COOL}/\text{L}_2\text{O}$	
$k_0^{\text{H}}$	H	H	}1.21 ± 0.30
$k_0^{\text{D}}$	D	H	
$k_0^{\text{H}}$	H	D	}1.08 ± 0.20
$k_0^{\text{D}}$	D	D	
$k_0^{\text{H}}$	H	H	}1.20 ± 0.10
$k_0^{\text{D}}$	H	D	
$k_0^{\text{H}}$	D	H	}1.07 ± 0.32
$k_0^{\text{D}}$	D	D	

<sup>a</sup> The symbol L refers to any isotope of hydrogen. The specific isotopic pair used to calculate each  $k_0^{\text{H}}/k_0^{\text{D}}$  is shown in italic type.

<sup>b</sup> The tabulated uncertainties in isotope effects are calculated from the uncertainties in rate constants in Table I.

Table III. Isotope Effects on  $k_{\text{H}_2\text{O}}$ <sup>a</sup>

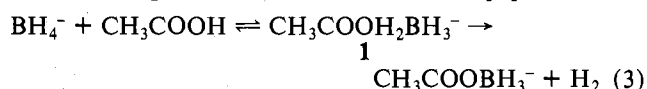
rate const	reactants		$k_{\text{H}_2\text{O}}^{\text{H}}/k_{\text{H}_2\text{O}}^{\text{D}}$
	$\text{BL}_4^-$	$\text{CH}_3\text{COOL}/\text{L}_2\text{O}$	
$k_{\text{H}_2\text{O}}^{\text{H}}$	H	H	}0.70 ± 0.05
$k_{\text{H}_2\text{O}}^{\text{D}}$	D	H	
$k_{\text{H}_2\text{O}}^{\text{H}}$	H	D	}0.88 ± 0.10
$k_{\text{H}_2\text{O}}^{\text{D}}$	D	D	
$k_{\text{H}_2\text{O}}^{\text{H}}$	H	H	}1.55 ± 0.08
$k_{\text{H}_2\text{O}}^{\text{D}}$	H	D	
$k_{\text{H}_2\text{O}}^{\text{H}}$	D	H	}1.96 ± 0.25
$k_{\text{H}_2\text{O}}^{\text{D}}$	D	D	

<sup>a</sup> See footnotes to Table II.

of  $k_0$  are not altogether random. If the errors in the values of  $k_0$  for the various isotopic combinations are in the same direction, then the actual uncertainties in the isotope effects in Table II are very much smaller than the tabulated values. The magnitudes of the isotope effects for the "spontaneous" reaction are highly uncertain, but it seems probable that all are greater than 1. Little more can be claimed for the data of Table II.

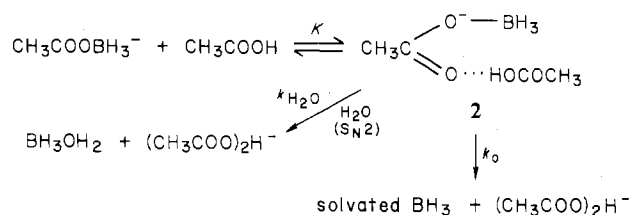
In many of the kinetic experiments a small residual concentration of reducing agent was observed after the kinetically measured reaction was complete. Absorbance due to this residual reducing agent was designated  $A_\infty$ . The residual reducing agent seems to be a relatively stable B-H compound, probably a  $\text{BH}_3$  derivative, formed in one of the reaction pathways available in the kinetically "spontaneous" breakdown of complex 2. The nature of the various intermediates between  $\text{BH}_4^-$  and the final product, boric acid, is dealt with elsewhere.<sup>1</sup> The rate constants are calculated from the slope in a linear plot of  $\log(A - A_\infty)$  vs. time.

**Reaction Mechanism.** The reversible formation of a complex, 1, and its breakdown directly to  $\text{CH}_3\text{COOBH}_3^-$ , as indicated in eq 3, are discussed in a concurrent paper.<sup>1</sup> Modler



and Kreevoy have used the behavior of the rate as a function of the acetic acid concentration to show that there must be an accumulation of a reversibly formed complex between acetic acid and some boron-hydrogen compounds and that the

Scheme I



breakdown of this complex is rate determining. That behavior has now been confirmed. They believed that loss of the first hydride from  $\text{BH}_4^-$  occurs in the rate-determining step, hence  $\text{BH}_4^-$  must be the boron compound in the accumulating complex. We have presented  $^{11}\text{B}$  NMR and kinetic data<sup>1</sup> which show that the boron compound in the accumulating complex is  $\text{CH}_3\text{COOBH}_3^-$ . All of the above, together with the data of Tables I and II, can be rationally accounted for by the reactions of eq 3 and Scheme I, assuming **2** to be the accumulating complex.

Scheme I gives to **2** the role previously assigned by Modler and Kreevoy to **1**. Otherwise, Scheme I exactly generates the same rate law postulated by Modler and Kreevoy, and their arguments in its favor remain valid, just as their values of rate and equilibrium constants remain relevant. The present work refines the rate constants but makes no dramatic changes in the overall picture, other than replacing **1** with **2**.

It is particularly significant that, in the presence of enough acetic acid to convert nearly all  $\text{CH}_3\text{COOBH}_3^-$  into **2** (an excess concentration of  $\text{CH}_3\text{COOH}$  of at least 0.02 M),<sup>2</sup> the reaction rate is essentially independent of acetic acid concentration, yet in the absence of acetic acid the  $\text{CH}_3\text{COOBH}_3^-$  is stable enough to persist for at least 13 days in solution.<sup>1</sup> The sodium salt of  $\text{CH}_3\text{COOBH}_3^-$  has been isolated as a solid compound.<sup>15</sup> The necessity for the presence of acetic acid in the breakdown of  $\text{CH}_3\text{COOBH}_3^-$  and the  $k_{\text{HA}}/k_{\text{DA}}$  greater than 1 for the "spontaneous" mechanism both require the direct participation of acetic acid in the rate-determining step. It is not readily distinguishable whether the rather substantial hydrogen isotope effect for acetic acid-water in the water-promoted mechanism is an acetic acid effect, a water effect, or a combination of the two. Rapid isotopic exchange between acetic acid and water makes it impossible to study separately the isotope effects for the two reagents in the water-promoted reaction, where the simultaneous presence of both is required. However, the isotope effect is quite consistent with what would be expected from the postulated transition state for cleavage of the B-O bond of **2**, in which acetic acid forms an incipient biacetate ion and exerts a "pulling" effect in cleaving the bond.<sup>16</sup>

Superimposed upon this isotope effect for substitution in the  $\text{OL}^{17}$  group of the acetic acid is a possible secondary effect for water in nucleophilic substitution. The origin of such effects is still unclear,<sup>18,19</sup> and they are not usually observed unless water is the solvent.<sup>18</sup> They are also quite a bit smaller than the overall effect observed in the present case.<sup>18,19</sup> Such effects will, therefore, not be further considered.

The value of  $k_{\text{BH}_4^-}/k_{\text{BD}_4^-}$  and the linear dependence of rate on water concentration both suggest nucleophilic attack on **2** by water in the water-promoted reaction. Llewellyn, Robertson, and Scott<sup>20</sup> report  $k_{\text{H}}/k_{\text{D}}$  ratios of 0.90-0.97 for the three methyl hydrogens in the solvolysis of methyl halides and esters in water, where the reaction must proceed via a bimolecular attack on the methyl carbon. These authors present a discussion and rationalization of the isotope effect which can also be applied to the present case in view of the structural similarity between  $\text{BH}_3\text{X}^-$  and  $\text{CH}_3\text{X}$ . More general discussions of  $\alpha$ -hydrogen isotope effects in methyl transfer reactions<sup>19</sup> and in aliphatic nucleophilic substitution<sup>21</sup> are also

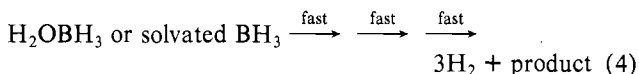
applicable to the present case. An inverse isotope effect implies that the constraints applied by the valence forces to the atoms undergoing isotopic substitution have been increased. In the case of nucleophilic methyl transfer the constraints on the bending motion of the C-H bonds increase on forming the transition state because the carbon is then making bonds, or partial bonds, to five ligands instead of four. It, therefore, becomes less free to accommodate the bending motions by rehybridization. Exactly the same reasoning can be applied to the present case if the reaction is regarded as a nucleophilic displacement on boron, and this strengthens our view that this is the case.

The observed kinetic isotope effects for the water-promoted reaction in acetonitrile, Table III, are remarkably similar to those observed for acid-catalyzed hydrolysis of  $\text{BH}_4^-$  in water solution.<sup>22-24</sup> The similarity in the effects of substitution on boron may occur because the role of these hydrogens in the present reaction is similar to that played by the three non-reacting hydrogens in the aqueous solution hydrolysis of  $\text{BH}_4^-$ .<sup>22</sup> The similarity of the effects of substitution in the hydroxylic position appears to be coincidental.

Figure 2 and Table III show a significant failure of the rule of the geometric mean; the effect of deuterium substitution at boron is reduced by making the hydroxylic hydrogens deuterium. The effect appears to be marginally outside of the experimental uncertainties. This may reflect the coupling of the vibrations of the two kinds of hydrogen.

The precise nature of the kinetically "spontaneous" path is much less clear. The  $^{11}\text{B}$  NMR evidence<sup>1</sup> suggests a considerable variety of products for this path, although that may be an artifact of the high concentration of  $\text{BH}_4^-$  and the rapid depletion of acetic acid in the NMR experiments. The first products probably are some form of solvated or complexed  $\text{BH}_3$ .

Little can be said with confidence about the fate of  $\text{BH}_3$  after the rate-determining step by either pathway. It appears that the cleavage of all B-H bonds is kinetically fast compared to the rate of cleavage of the B-O bond in **2**, since the evidence<sup>1,2</sup> points to  $\text{CH}_3\text{COOBH}_3^-$  in rapid equilibrium with **2**, as the only accumulating intermediate in the overall reaction. The B-H bonds almost certainly are cleaved in successive stages (eq 4) leading to the final product, boric acid



under kinetic conditions, borate ion in the quenched solutions, or a mixture of both under some conditions of low water concentration.<sup>1</sup> There is some NMR evidence,<sup>1</sup> which is by no means conclusive, that after the rate-determining step each successive B-H bond cleavage is faster than the preceding.

The identified steps in the overall acidolysis of  $\text{BH}_4^-$  in moist acetonitrile are given in eq 3 and Scheme I, with the remaining steps occurring in three stages (eq 4) by unknown mechanisms. The value of  $K$  (Scheme I) has been determined previously.<sup>2</sup> Improved values of  $k_0$  and  $k_{\text{H}_2\text{O}}$  for various combinations of H and D in the reactants are reported in Table I. Future identification of the more abundant of the "downstream" intermediates detected by  $^{11}\text{B}$  NMR, but not yet identified, may shed much light on the mechanism of the "spontaneous" reaction pathway.

**Kinetic Method.** Earlier studies in this laboratory<sup>2</sup> utilized borohydride as its tetraethylammonium salt. Aliquots of the reaction mixture were analyzed by measuring the absorbance of NADH formed in the reduction of  $\text{NAD}^+$  by unreacted hydridic boron compounds in the quenched aliquots. The procedure used in the present study has several marked advantages. Tetraalkylammonium salts are quite hygroscopic and, on that account, pose some problems in handling, par-

ticularly in weighing. The (Ph<sub>3</sub>P)<sub>2</sub>N<sup>+</sup>BH<sub>4</sub><sup>-</sup> is not noticeably hygroscopic, is high in molecular weight, permitting greater precision in weighing small quantities of borohydride, is very soluble in organic solvents, and, for the purpose of this study, is adequately soluble in 4:1 water-acetonitrile mixed solvent.

For analysis NAD<sup>+</sup> has several serious disadvantages. Not only is the price high but it has limited shelf life, even when stored in a freezer. At the wavelength of 340 nm, at which the absorbance of NADH is measured, there is not a true absorption maximum but rather a shoulder, so the absorbance is rather sensitive to small changes in the wavelength of measurement. Furthermore, at this wavelength, unreacted NAD<sup>+</sup> has a weak, but measurable, absorbance. Measured absorbances are, therefore, slightly sensitive to the concentration of unreacted NAD<sup>+</sup>. The BNA<sup>+</sup> ion suffers from none of these disadvantages. BNA<sup>+</sup>Cl<sup>-</sup> is inexpensive, easy to make, and stable, at least in the solid state. At 358 nm unreacted BNA<sup>+</sup> does not absorb measurably, and (BNA)H shows a relatively broad absorption maximum, making the measured absorbance independent of unreacted BNA<sup>+</sup> and insensitive to small changes in the wavelength of measurement. At 358 nm the absorptivity of (BNA)H is about 15% higher than that of NADH at 340 nm, a small but significant advantage.

Overall, the change to the more desirable reagents discussed above, together with the careful elimination of catalytic impurities, has resulted both in a substantial reduction in scatter in the kinetic measurements of series I (see Table I) and, over the range of water concentrations used in the study, in an average lowering of about 20% in the magnitude of observed rate constants.

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**Registry No.** (Ph<sub>3</sub>P)<sub>2</sub>N<sup>+</sup>BH<sub>4</sub><sup>-</sup>, 65013-26-5; (Ph<sub>3</sub>P)<sub>2</sub>N<sup>+</sup>BD<sub>4</sub><sup>-</sup>, 70479-83-3; BH<sub>4</sub><sup>-</sup>, 16971-29-2; CH<sub>3</sub>COOH, 64-19-7.

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## Magnetic Interactions in Exchange-Coupled Pairs of Chromium(III) and Molybdenum(III) Ions in Crystals of CsMX<sub>3</sub> Halides

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Trivalent ions tend to cluster in pairs when introduced as impurities into crystals of CsMX<sub>3</sub> salts such as CsMgCl<sub>3</sub>, CsMgBr<sub>3</sub>, and CsCdBr<sub>3</sub>. Pairs of this type which contain two paramagnetic trivalent ions behave as magnetic dimers. The EPR spectra of the Cr(III)-Cr(III) and Mo(III)-Mo(III) pairs which are formed in these crystals have been carefully analyzed. The analysis is based on exact solutions of a spin Hamiltonian written for systems which contain two magnetically coupled  $S = 3/2$  ions. In all cases accurate spectral descriptions are obtained. The magnetic interactions between metal ions are accurately characterized by two linear exchange terms:  $J\vec{S}_1\vec{S}_2 + D_e(3\vec{S}_{1z}\vec{S}_{2z} - \vec{S}_1\vec{S}_2)$ . In these systems the exchange interactions appear to be antiferromagnetic with  $J$  values which range from 1 to 6 cm<sup>-1</sup>.

### Introduction

Electron paramagnetic resonance studies indicate that trivalent ions tend to cluster in pairs when doped into crystals of CsMX<sub>3</sub> salts which are known to adopt the linear chain CsNiCl<sub>3</sub> structure.<sup>1-4</sup> Even at doping levels lower than one part per thousand it appears that a majority of the trivalent impurities enter the CsMX<sub>3</sub> crystals in pairs. This unusual tendency arises from the rather strict charge compensation requirement of the linear chain lattice. The CsNiCl<sub>3</sub> structure

can be described as an array of parallel linear chains composed of MX<sub>6</sub><sup>4-</sup> octahedra sharing opposite faces. These chains are anionic and have the stoichiometry [MX<sub>3</sub><sup>-</sup>]<sub>n</sub>. The cesium ions occupy positions between the chains and balance the anionic charge. When trivalent impurities enter crystals of this type, two impurity ions associate with a divalent ion vacancy within a single [MX<sub>3</sub><sup>-</sup>]<sub>n</sub> chain (see Figure 1). The combination of the two impurities with a vacancy provides a means by which trivalent ions can be incorporated into the [MX<sub>3</sub><sup>-</sup>]<sub>n</sub> chains