

Na[UF<sub>6</sub>], 18918-89-3; K[UF<sub>6</sub>], 18918-88-2; [C<sub>6</sub>H<sub>5</sub>N(CH<sub>3</sub>)<sub>3</sub>][UF<sub>6</sub>], 71032-36-5; [(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>PNP(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>][UF<sub>6</sub>], 71032-37-6; Na[U(O-C<sub>2</sub>H<sub>5</sub>)<sub>6</sub>], 71032-38-7; [Bu<sub>4</sub>N][UCl<sub>6</sub>], 30723-72-9; UCl<sub>5</sub>, 13470-21-8.

**Supplementary Material Available:** The infrared spectra of UF<sub>5</sub>·CH<sub>3</sub>CN and UF<sub>5</sub>(CH<sub>3</sub>CN)<sub>x</sub> and the near-infrared visible spectra of UF<sub>5</sub> in DME, ethanol, and nitromethane and a table of near-infrared visible absorption frequencies for Na[UF<sub>6</sub>] and for UF<sub>5</sub> in acetonitrile, benzonitrile, Me<sub>2</sub>SO, DMF, CH<sub>3</sub>NO<sub>2</sub>, DME, and ethanol (4 pages). Ordering information is given on any current masthead page.

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## Mechanism of the Reaction between Vanadium(III) Ions and *p*-Aminosalicylic Acid

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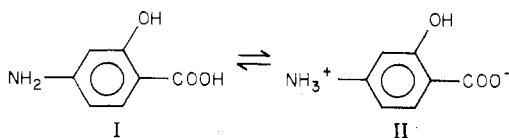
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The kinetics of the vanadium(III)-*p*-aminosalicylic acid (H<sub>2</sub>L<sub>T</sub>) system have been investigated at 25 °C and an ionic strength of 1 M, by use of the stopped-flow technique. Rate constants for the reaction between V<sup>3+</sup> and HL<sup>-</sup> and H<sub>2</sub>L<sup>+</sup> have been measured, and limits for the rate constants involving the proton-ambiguous, nonpolar H<sub>2</sub>L and zwitterion H<sub>2</sub>L<sup>±</sup> have been estimated. The dependence of the rate constant on the basicity of the ligand confirms the associative mechanism suggested earlier. An additional argument in favor of this mechanism is provided by the value of *k*<sub>HL<sup>-</sup></sub>, 7 × 10<sup>3</sup> M<sup>-1</sup> s<sup>-1</sup>, which is higher than would be compatible with the alternative, dissociative, reaction path.

### Introduction

We have recently<sup>1</sup> studied the kinetics of the complex formation between V<sup>3+</sup> and salicylic acid. Our results tended to confirm the associative mechanism suggested by previous authors.<sup>2-4</sup> A further investigation of the kinetics of reactions involving V<sup>3+</sup> seemed, however, desirable. Again<sup>5</sup> with the aim of comparing ligands which have identical reactive sites and differ only in their basic strength, we chose *p*-aminosalicylic acid.

The system investigated exhibits some special features since, like all amino acids, our ligand in its neutral form may be assumed to exist partly as a nonpolar molecule H<sub>2</sub>L (I) and partly as a zwitterion H<sub>2</sub>L<sup>±</sup> (II). This creates a new kind of proton ambiguity.



We shall write H<sub>2</sub>L<sub>T</sub> when we do not wish to differentiate between the two forms. Clearly, [H<sub>2</sub>L<sub>T</sub>] = [H<sub>2</sub>L] + [H<sub>2</sub>L<sup>±</sup>].

### Experimental Section

The *p*-aminosalicylic acid used was from Aldrich Chemical Co. ("analyzed"). Stock solutions in excess sodium hydroxide were stored

under refrigeration for not more than a few days and were checked spectrophotometrically for possible decarboxylation.<sup>7</sup> Solutions of V(III) were prepared as described previously.<sup>1</sup>

The kinetic results were again<sup>1</sup> obtained by the stopped-flow technique; all the experimental methods were those described in our previous paper.<sup>1</sup> The temperature was 25 °C throughout, and the ionic strength was 1 M.

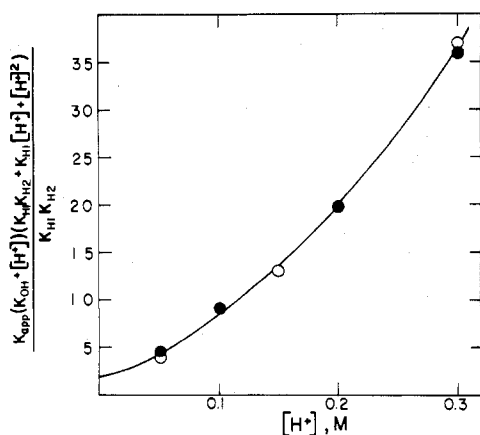
The concentrations of the cation, *a*, ranged between 2 × 10<sup>-3</sup> and 3 × 10<sup>-2</sup> M and were in excess over those of the ligand, *b*, which ranged between 10<sup>-4</sup> and 7.5 × 10<sup>-4</sup> M. All experiments were carried out at a wavelength of 325 nm, where the difference in absorption between the complex and the sum of the absorptions of *p*-aminosalicylic acid and of V(III) solutions, at the same concentration and pH, was at its maximum.<sup>1</sup>

### Results

**Equilibrium Constants.** We again<sup>1,5</sup> define an apparent, [H<sup>+</sup>]-dependent, formation constant of our complex, namely

$$K_{\text{app}} = \frac{[\text{complex}]}{[\text{V(III)}][\text{H}_3\text{L}^+] + [\text{H}_2\text{L}_T] + [\text{HL}^-]} = \frac{[\text{complex}]}{\{[\text{complex}]K_{\text{H}_1}K_{\text{H}_2}[\text{H}^+]\} / \{[\text{V}^{3+}][\text{HL}^-](K_{\text{H}_1}K_{\text{H}_2} + K_{\text{H}_1}[\text{H}^+] + [\text{H}^+]^2)(K_{\text{OH}} + [\text{H}^+])\}} \quad (\text{I})$$

where *K*<sub>H1</sub> and *K*<sub>H2</sub> are the dissociation constants of H<sub>3</sub>L<sup>+</sup> and of H<sub>2</sub>L<sub>T</sub>, respectively, and *K*<sub>OH</sub> is the hydrolysis constant of V<sup>3+</sup>.



**Figure 1.** Dependence of  $[K_{app}(K_{H1}K_{H2} + K_{H1}[H^+] + [H^+]^2)(K_{OH} + [H^+])]/(K_{H1}K_{H2})$  on  $[H^+]$  (see eq I): dots, kinetic results; open circles, spectrophotometric results.

At three hydrogen ion concentrations, namely, 0.05, 0.15, and 0.30 M,  $K_{app}$  was measured spectrophotometrically as described before.<sup>1,5</sup>

At four hydrogen ion concentrations, namely, 0.05, 0.10, 0.20, and 0.30 M,  $K_{app}$  was evaluated from kinetic measurements, with the aid of the relationship

$$k_{obsd} = k_f \bar{a} + k_d \quad (II)$$

where  $\bar{a}$  is a suitably weighted mean of the sum of the reactant concentrations (and differs significantly from  $a$ ),  $k_{obsd}$  is the observed, pseudo-first-order, rate constant, and  $k_f$  and  $k_d$  are the  $[H^+]$ -dependent rate constants for formation and decomposition of the complex, respectively. Straight lines were obtained when  $k_{obsd}$  was plotted against  $\bar{a}$ . The slope and intercept yield  $k_f$  and  $k_d$ , respectively; their ratio equals  $K_{app}$ .<sup>8</sup>

When  $[K_{app}(K_{H1}K_{H2} + K_{H1}[H^+] + [H^+]^2)(K_{OH} + [H^+])]/(K_{H1}K_{H2})$  is plotted as a function of  $[H^+]$  (with  $K_{H1} = 1.12 \times 10^{-2}$  M,<sup>9</sup>  $K_{H2} = 2.09 \times 10^{-4}$  M,<sup>9</sup> and  $K_{OH} = 1.4 \times 10^{-3}$  M<sup>10</sup>), Figure 1 is obtained. A parabola can be fitted to the experimental points; the expression  $[\text{complex}][H^+]/[V^{3+}][HL^-]$  must therefore be of the form  $K_1 + K_1'[H^+] + K_1''[H^+]^2$  (see eq 1) and three complexes are formed. The regression coefficients of Figure 1 are

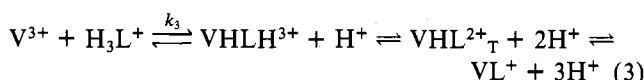
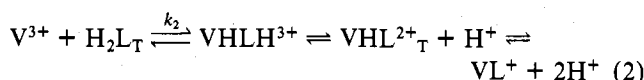
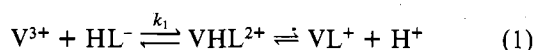
$$K_1 = \frac{[VL^+][H^+]}{[V^{3+}][HL^-]} = (1.91 \pm 0.9) \times 10^4$$

$$K_1' = \frac{[VHL^{2+}_T]}{[V^{3+}][HL^-]} = (4.0 \pm 1.3) \times 10^5 \text{ M}^{-1}$$

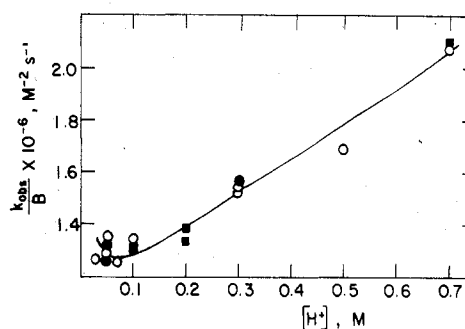
$$K_1'' = \frac{[VHLH^{3+}]}{[V^{3+}][HL^-][H^+]} = (2.52 \pm 0.35) \times 10^6 \text{ M}^{-2}$$

(We have written  $VHL^{2+}_T$  in order to indicate that this substance may be a mixture of  $VHL^{2+}$  and  $VLH^{2+}$ , the proton being part of the OH or  $NH_3^+$  groups, respectively.)

**Rate Constants.** We assume the complexes to be formed by three parallel reaction paths, namely, eq 1-3. Since

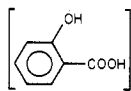
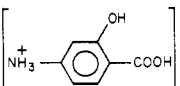
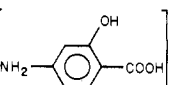
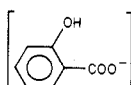
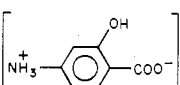
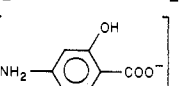


$VOH^{2+}$  is present at much lower concentration than  $V^{3+}$  and



**Figure 2.** Dependence of  $k_{obsd}/B$  on  $[H^+]$  (see eq III and IV). Dots represent two experiments each, and full squares, three experiments.

**Table I.** Rate Constants for Substitution on  $V^{3+}$  at 25 °C

ligand	$pK_H^a$	$k$ , $M^{-1} s^{-1}$	ref
$Cl^-$	$\leq 3$		3
$Br^-$	$\leq 10$		3
$H_2Sal$ 		4.9	1
$H_3L^+$ 		3.3	b
$H_2L$ 		3.3-25	b
$HN_3$		(0.4)	12
$NCS^-$	$< 0^c$	104	11
		114	2
$H_2O$	-1.74	180	25
$HC_2O_4^-$	1.20	$1.3 \times 10^3$	3
$HSal^-$ 		2.80	$1.4 \times 10^3$
$H_2L^{\pm}$ 		2.84-3.44	$(1.6-7) \times 10^3$
$HL^-$ 		3.60	$7 \times 10^3$
$N_3^-$		4.15	$(9 \times 10^3)$

<sup>a</sup> Dissociation constants of the acids conjugate to the active sites of the ligands. <sup>b</sup> This work. <sup>c</sup> Reference 14b.

since  $VOH^{2+}$  has previously been found not to be more reactive than  $V^{3+}$ ,<sup>1-3</sup> we omit in our scheme the reaction between  $VOH^{2+}$  and  $H_2L_T$  which has the same  $[H^+]$  dependence as reaction 1. Furthermore, we omit the additional proton-ambiguous pair of reactions involving  $V^{3+} + L^{2-}$  and  $VOH^{2+} + HL^-$ , for which we found no experimental evidence.

If we assume all the protolytic equilibria to be again rapid,<sup>1</sup> we can write

$$k_{obsd} = [k_1/[H^+] + k_2/K_{H2} + k_3[H^+]/(K_{H1}K_{H2})] \times B \quad (III)$$

with

$$B = \frac{(K_{app}\bar{a} + 1)[H^+]^2}{K_1 + K_1'[H^+] + K_1''[H^+]^2} \quad (IV)$$

A plot of  $k_{obsd}/B$  as a function of  $[H^+]$  is shown in Figure 2, for 30 experiments, at  $[H^+]$  between 0.03 and 0.70 M. This is obviously not a straight line. We therefore treated  $k_{obsd}/B$

as a linear regression in two variables,  $[H^+]$  and  $1/[H^+]$ , in accordance with the expression in brackets in eq III. The regression coefficients yield  $k_1 = (7.0 \pm 1.6) \times 10^3$ ,  $k_2 = 226 \pm 6$ , and  $k_3 = 3.3 \pm 0.1 \text{ M}^{-1} \text{ s}^{-1}$ .

### Discussion

If we want to compare our rate constants with those obtained for other systems<sup>1-3,11,12</sup> involving  $V^{3+}$ , we have to remember that  $H_2L_T$  is a mixture of  $H_2L$  and  $H_2L^\pm$ . We are chiefly interested in the dissociation constants of the carboxylic group. For  $H_3L^+$ , this quantity is not equal to  $K_{H1}$  but rather to  $K_{H1}K_D/(1 + K_D)$ , where<sup>13</sup>

$$K_D = [H_2L^\pm]/[H_2L] \quad (V)$$

Similarly, the dissociation constant of the carboxylic group in  $H_2L$  is not  $K_{H2}$ , but  $K_{H2}(1 + K_D)$ .

Clearly,  $K_D$  is needed for our discussion. A method for estimating  $K_D$  is based<sup>13</sup> on the assumption that the acid dissociation constant of the  $NH_3^+$  group should be the same in the amino acid and its ethyl or methyl esters. Actually, it is reasonable to assume that it is somewhat higher. An estimate based on this assumption would then provide an upper limit for  $K_D$ . Unfortunately, no data on esters of *p*-aminosalicylic acid seem to be available.<sup>14</sup> If we assume it to be similar to *p*-aminobenzoic acid (for which the ratio between  $K_{H1}$  and the dissociation constant of the ester is<sup>13</sup> 1.148), we get an approximate upper limit of 0.15 for  $K_D$ .

What is probably a lower limit for  $K_D$  can be obtained from the assumption that the rate constants for complex formation by the  $COO^-$  and  $COOH$  groups are either uninfluenced or—more probably—somewhat reduced by the protonation of the amino group. This means that

$$k_{H_2L^\pm} \leq k_1 \quad \text{and} \quad k_{H_2L} \geq k_3 \quad (VI)$$

Now, reaction 2 is the sum of two proton-ambiguous paths involving  $H_2L^\pm$  and  $H_2L$ ; therefore

$$k_2 = k_{H_2L^\pm}K_D/(1 + K_D) + k_{H_2L}/(1 + K_D) \quad (VII)$$

which, on the above assumption, yields  $K_D \geq 3 \times 10^{-2}$ . Both estimates, though ranging between the rather wide limits of  $3 \times 10^{-2}$  and 0.15, concur in establishing  $H_2L$  as the predominant species.

Therefore, when  $K_D$  is varied within the above limits, the dissociation constant of the carboxylic hydrogen in  $H_2L$  remains almost unaffected. On the other hand, the estimate for the corresponding dissociation constant of  $H_3L^+$  depends very strongly on the choice of  $K_D$ . The result is shown in Table I.

In this table, we present all the kinetic data available for substitution reactions on  $V^{3+}$ , including our results. The ligands are arranged in order of increasing basicity of the reactive site. The dissociation constants of the corresponding conjugate acids are also shown in the table.

The upper limit for  $k_{H_2L^\pm}$  is based on the inequality (VI). Another estimate for this upper limit can be obtained by putting  $k_{H_2L}$  in eq VII equal to zero. The value of  $k_{H_2L^\pm}$  thus obtained depends on the value of  $K_D$  adopted and varies between the limits shown in the table. It turns out that, when  $k_{H_2L}$  is not put equal to zero but is assumed to have a reasonable value (see below), the result for  $k_{H_2L^\pm}$  would be little affected. The value obtained with the higher value of  $K_D$  may therefore be considered the lower limit.

As for  $k_{H_2L}$ , the lower limit shown is obtained from the inequality (VI). The upper limit obtained by putting  $k_{H_2L^\pm}$  in eq VII equal to zero, namely,  $(2.3-2.6) \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$ , seems unreasonably high. A more realistic assumption is based on

a comparison between salicylic and aminosalicylic acids. If we assume that  $k_{H_2L}/k_{H_2Sal}$  equals  $k_{HL^-}/k_{HSal}$ , the value given in the table is obtained.

Our table shows that the rate constants are strongly ligand dependent. This confirms the previous assumption<sup>1-4</sup> of an associative mechanism.

Our table further shows that the property which chiefly determines the rate constant is the basicity of the ligand.

For instance,  $HL^-$  is a stronger base than  $HSal^-$  by a factor of about 7 and has a rate constant which is higher by a factor of about 5.

Furthermore—provided we accept the higher of the two estimates for  $K_D$ —the carboxylic groups in  $H_3L^+$  and  $H_2Sal$  have similar basicities. The rate constants for these acids are also similar—although what difference there is lies in the direction opposite to that which we should expect. It is possible that the positive charge on  $H_3L^+$ , though removed from the reactive site and therefore often ignored,<sup>15-17</sup> should nevertheless somewhat retard the reaction with a three-positive partner.

Similarly, the rate constant for  $H_2L^\pm$  is between those of  $HSal$  and  $HL^-$ , and so are the basicities of these species.

The results for  $HN_3$  and  $N_3^-$  are given in parentheses since they were calculated from the rate constant of the back-reaction and an equilibrium constant which is very low and therefore not measurable with sufficient accuracy.<sup>12</sup>

The strong correlation between the rate constant and the basicity of the incoming ligand is in line with the fact that the  $V^{3+}$  ion has the characteristics of a "hard acid".<sup>18,19</sup> The behavior of  $V^{3+}$  toward nucleophilic substitution thus fits the rule that hard acids are sensitive to the basicity of the incoming nucleophile.<sup>20</sup>

A further argument<sup>21</sup> against the dissociative Eigen mechanism can be deduced from the value of  $k_{HL^-}$ , the highest value reported for substitution on  $V^{3+}$ . If complex formation proceeded according to that mechanism,  $k_{HL^-}$  would be equal to  $k^*K_{out}$ , where  $k^*$  is the first-order rate constant for the exchange between water and ligand in the inner coordination sphere and  $K_{out}$  is the outer-sphere association constant. Taking  $K_{out}$  equal to  $\sim 1 \text{ M}^{-1}$  at our ionic strength<sup>22</sup> would lead to a value of  $k^*$  of  $7 \times 10^3 \text{ s}^{-1}$ . This exceeds the value of  $\sim 1.2 \times 10^3 \text{ s}^{-1}$  calculated<sup>23,24</sup> from the rate of water exchange as measured directly by the method of NMR.<sup>25</sup> As a rule, the rate of complex formation is somewhat lower than that calculated from water exchange. On the other hand, no incompatibility with the measured rate of water exchange arises on the basis of the associative mechanism. The second-order rate constant for the substitution of water by water (see Table I) is entirely in line with the rate constant for the substitution of water by other ligands.

**Registry No.**  $V^{3+}$ , 22541-77-1;  $H_2L$ , 65-49-6;  $H_3L^+$ , 40853-19-8;  $HL^-$ , 769-50-6.

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## Reexamination of the Mechanism of Acid-Catalyzed Amine-Borane Hydrolysis. The Hydrolysis of $\text{NH}_3\cdot\text{BH}_3$

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Studies of the acid-catalyzed hydrolysis of ammonia-borane confirm the trend  $k_2(\text{NH}_3\cdot\text{BH}_3) > k_2(\text{MeNH}_2\cdot\text{BH}_3) > k_2(\text{Me}_2\text{NH}\cdot\text{BH}_3) > k_2(\text{Me}_3\text{N}\cdot\text{BH}_3)$  where  $k_2 = -(1/[\text{H}^+]) \text{d} \ln [\text{R}_3\text{NBH}_3]/\text{d}t$ . Unlike the behavior of  $\text{Me}_3\text{N}\cdot\text{BH}_3$ , hydrolysis of  $\text{NH}_3\cdot\text{BH}_3$  (at pH 4–5) is faster than boron-bonded hydrogen exchange. A comparison of rates in acetate and deuterated acetate buffer solutions shows a normal solution isotope effect ( $k_{\text{H}_2\text{O}}/k_{\text{D}_2\text{O}} \approx 1.5$ ). This is approximately the same as that observed for  $\text{Me}_3\text{N}\cdot\text{BH}_3$  ( $\text{Me}_3\text{N}\cdot\text{BD}_3$ ) in 0.29 M  $\text{H}_2\text{SO}_4$  ( $\text{D}_2\text{SO}_4$ ). Results are interpreted to be consistent with a previously suggested mechanism involving cis displacement of  $\cdot\text{BH}_3$  via electrophilic attack of the proton of a general acid at amino nitrogen (the nitrogen-boron electron pair). An alternative mechanism involving reversible protonation of substrate to a five-coordinate boron species with subsequent loss of  $\text{H}_2$  cannot be precluded, but difficulties persist in efforts to reconcile such a model with kinetic effects, particularly those of *N*-alkyl substitution and relative rates of hydrolysis and substrate-solvent hydrogen exchange.

Previous investigations have shown amine-boranes ( $\text{BH}_3$  adducts of nitrogen bases) to undergo both uncatalyzed and acid-catalyzed solvolysis in mixed aqueous solvents.<sup>1–3</sup> Mechanistic models for both pathways have been proposed, that for the acid-dependent reaction involving rate-determining cis displacement of  $\text{BH}_3$  via electrophilic attack by the proton of a general acid at amino nitrogen, i.e., at the nitrogen-boron electron pair. Various solvent and substituent effects observed for the hydrolysis of substituted phenylamine-boranes in aqueous dioxane as well as of alkylamine-boranes in water have been interpreted in terms of this mechanism.<sup>1,4</sup> More recently, and after extensive studies of the hydrolysis of tetrahydridoborate,  $\text{BH}_4^-$ ,<sup>5–12</sup> and cyanotrihydroborate,  $\text{BH}_3\text{CN}^-$ , in which five-coordinate boron species  $\text{H}_2\text{BH}_3$  and  $\text{H}_2\text{BH}_2\text{CN}$  have been proposed as reaction intermediates, it has been suggested that analogous species are involved as intermediates in the hydrolysis of amine-boranes.<sup>12,13</sup> The present study of ammonia-borane, originally undertaken to provide additional data on effects of *N*-substitution on rates of amine-borane hydrolysis, provides an opportunity to reconsider both mechanistic models.

### Experimental Section

**Materials and Apparatus.** Ammonia-borane was supplied by the Callery Chemical Co. Analysis was carried out by using hydrolytic and titrimetric procedures.<sup>14</sup> Anal. Calcd for  $\text{NH}_3\cdot\text{BH}_3$  (30.865): H (hydridic), 9.80; B, 35.02; N, 45.38. Found: H (hydridic), 9.9; B, 34.4; N, 44.8. The purity is improved through vacuum sublimation. Trimethylamine-borane was obtained from Aldrich Chemical Co. and sublimed in vacuo. Distilled deionized water was used to prepare all aqueous solutions. Deuterium oxide (99.8 atom % D) and deuteriosulfuric acid (>98%  $\text{D}_2\text{SO}_4$  in  $\text{D}_2\text{O}$ ) were obtained from Diaprep, Inc., and deuterium chloride was prepared according to the method of Brown and Groot.<sup>15</sup> Deuterated acetate buffer solutions were prepared through addition of deuterium oxide solutions of DCl to  $\text{D}_2\text{O}$  solutions of anhydrous sodium acetate. Infrared spectra were obtained by using a Beckman IR 4250 spectrophotometer. Kinetic studies were carried out by using Sargent Thermonitor and Freas Precision constant-temperature baths controlled to  $\pm 0.05^\circ\text{C}$ .

**Kinetic Studies and Deuterium Exchange.** Samples of  $\text{NH}_3\cdot\text{BH}_3$  (20–30 mg) and specific buffer solutions (100 mL) were brought to temperature equilibrium in separate flasks, and  $t_0$  was taken at the

Table I. Rates of Hydrolysis of  $\text{NH}_3\cdot\text{BH}_3$ ,  $\mu = 0.3$ ,  $t = 25^\circ\text{C}$

pH <sup>a</sup>	pD <sup>b</sup>	$10^5 k_{\text{obsd}}^c$
4.30 <sup>d</sup>		24.6
4.30 <sup>e</sup>		24.2
4.30 <sup>f</sup>		23.2
	4.40	16.9
4.6 <sup>g</sup>		13.7
4.76		11.1
	4.82	7.58
4.92		6.37
	5.0 <sup>h</sup>	3.6
	5.04	3.34
5.20		4.10
	5.20	2.84
	5.39	1.00
5.46		2.34
5.80		0.864
	5.90	0.883
6.10		0.553
		0.576 <sup>i</sup>
		0.605 <sup>j</sup>
		0.598 <sup>k</sup>
	6.12	0.307

<sup>a</sup> HOAc/OAc<sup>-</sup> buffer at pH 4.3–5.5;  $\text{H}_2\text{PO}_4^-/\text{HPO}_4^{2-}$  buffer at pH 5.8–6.1. <sup>b</sup> DOAc/OAc<sup>-</sup> buffer. <sup>c</sup>  $k_{\text{obsd}} = -\text{d} \ln [\text{NH}_3\cdot\text{BH}_3]/\text{d}t$ . <sup>d</sup>  $[\text{HOAc}] = 0.3 \text{ M}$ . <sup>e</sup>  $[\text{HOAc}] = 0.12 \text{ M}$ . <sup>f</sup>  $[\text{HOAc}] = 0.03 \text{ M}$ . <sup>g</sup>  $[\text{HOAc}] \approx [\text{OAc}^-] \approx 0.3 \text{ M}$  ( $\mu = 0.6$ ). <sup>h</sup>  $[\text{DOAc}] \approx [\text{OAc}^-] \approx 0.3 \text{ M}$  ( $\mu = 0.6$ ). <sup>i</sup>  $[\text{H}_2\text{PO}_4^-] = 0.053 \text{ M}$ . <sup>j</sup>  $[\text{H}_2\text{PO}_4^-] = 0.079 \text{ M}$ . <sup>k</sup>  $[\text{H}_2\text{PO}_4^-] = 0.105 \text{ M}$ .

time of mixing. Solution of  $\text{NH}_3\cdot\text{BH}_3$  was complete within 3 s. At selected time intervals, 10-mL samples of hydrolysate were withdrawn and iodometrically analyzed for soluble hydride.<sup>16</sup> A similar procedure was employed for the study of trimethylamine-borane hydrolysis in  $\text{H}_2\text{SO}_4$  and  $\text{D}_2\text{SO}_4$ . In separate experiments in which the extent of deuterium exchange in ammonia-borane was to be examined, a 280-mg sample of hydride was dissolved in 100 mL of deuterated acetate buffer (0.3 M DOAc, 0.3 M OAc<sup>-</sup>, pD 5). The course of hydrolysis was determined by periodic hydride analysis of 1-mL samples of hydrolysate. After about 23% hydrolysis, and again after 56% hydrolysis, a 40-mL sample was withdrawn and the reaction quenched by dropwise addition of 2 M NaOD (prepared by dissolving 4 g of NaOH in 50 mL of  $\text{D}_2\text{O}$ ) to adjust pD  $\approx 8$ . The solution was then saturated with NaCl and extracted three times with 40-mL