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Kinetic Study of Proton Exchange between the $\text{Al}(\text{OH}_2)_6^{3+}$ Ion and Water in Dilute Acid. Participation of Water Molecules in Proton Transfer¹

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Abstract: Rates of proton exchange between $\text{Al}(\text{OH}_2)_6^{3+}$ and H_2O were measured by nuclear magnetic resonance techniques in dilute solution between 0 and 50° and in the pH range 3.3–0.5. Proton exchange results largely from proton transfer rather than from the exchange of whole water molecules. Two kinetic processes were found: acid dissociation of $\text{Al}(\text{OH}_2)_6^{3+}$, and reaction between $\text{Al}(\text{OH}_2)_6^{3+}$, $\text{Al}(\text{OH}_2)_5\text{OH}^{2+}$, and two or more water molecules. The rate constant for acid dissociation, $1.1 \times 10^5 \text{ sec}^{-1}$ at 30°, is in close agreement with results obtained by the dissociation field method. Kinetic analysis and HOD– D_2O solvent isotope effects show that acid dissociation is a bimolecular process in which the proton is transferred directly to an adjacent water molecule; e.g., $(\text{D}_2\text{O})_5\text{Al}(\text{ODH}) + \text{OD}_2 \rightarrow (\text{D}_2\text{O})_5\text{AlOD} + \text{HOD}_2^+$. The specific rate of acid dissociation increases slightly with the chloride concentration. The second process is formulated conveniently as a symmetrical proton transfer involving hydrated $\text{Al}(\text{OH}_2)_6^{3+}$ and hydrated $(\text{H}_2\text{O})_5\text{AlOH}^{2+}$. In H_2O , this process appears to be diffusion controlled; the rate constant is high, $9 \times 10^8 \text{ sec}^{-1} M^{-1}$ at 30°, and the kinetic isotope effect in HOD– D_2O solvent is fairly small. One of the steps in the kinetic scheme is the dissociation of the hydrogen-bonded hydration complex, $(\text{H}_2\text{O})_5\text{Al}(\text{OH}) \cdot \text{H}^*\text{OH}$. The rate constant for breaking the $\text{Al}(\text{OH}) \cdot \text{H}^*\text{OH}$ hydrogen bond in this process is found to be $4 \times 10^7 \text{ sec}^{-1}$ at 30°. Because of the difference in the participation by water molecules in the two processes, the kinetics for proton exchange is complex; rates are not simply the sum of additive contributions from two separate processes.

It is well known that aluminum ion in aqueous solution exerts a marked effect on the properties of surrounding water molecules. This is shown, for example, by the partial molar volume of Al^{3+} , which has the astonishing value of $-46.7 \text{ cm}^3/\text{mole}$ in water at 22°.² The water molecules nearest the aluminum ion form a tight complex, $\text{Al}(\text{OH}_2)_6^{3+}$, whose composition has been demonstrated directly by nuclear magnetic resonance (nmr) experiments.^{3,4} Exchange of water molecules between this

complex and bulk solvent is relatively slow.^{3–6} In 0.5 M HClO_4 , the half-life is 6 sec at 25° and the activation energy is 27 kcal/mole;³ near pH 3, the half-life is greater than 0.02 sec.⁶

The proton nmr spectrum of $\text{Al}(\text{OH}_2)_6^{3+}$ in aqueous solution at low temperatures consists of a single line, consistent with an octahedral structure.⁴ Moreover, the $\text{Al}(\text{OH}_2)_6^{3+}$ ion is stable in the presence of anions such as Cl^- , NO_3^- , or ClO_4^- .^{3–6} For example, there is no detectable replacement of H_2O by Cl^- even when the ratio of Cl^- to H_2O in the bulk solvent is as high as 1:4.⁴

While the binding of six water molecules is especially

(1) Work supported by the Petroleum Research Fund of the American Chemical Society. Grateful acknowledgment is made to the donors of that fund.

(2) R. Zana and E. Yeager, *J. Phys. Chem.*, **71**, 521 (1967).

(3) R. E. Connick and D. N. Fiat, *J. Chem. Phys.*, **39**, 1349 (1963); D. Fiat and R. E. Connick, *J. Amer. Chem. Soc.*, **90**, 608 (1968).

(4) (a) R. Schuster and A. Fratiello, *J. Chem. Phys.*, **47**, 1554 (1967);

(b) A. Takahashi, *J. Phys. Soc. Japan*, **24**, 657 (1968).

(5) J. A. Jackson, J. F. Lemons, and H. Taube, *J. Chem. Phys.*, **32**, 553 (1960).

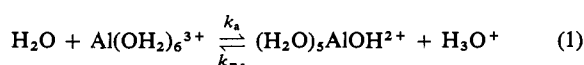
(6) H. W. Baldwin and H. Taube, *ibid.*, **33**, 206 (1960).

strong, the kinetic unit formed by the aluminum ion is larger than a hexahydrate. The van der Waals radius of $\text{Al}(\text{OH}_2)_6^{3+}$ is 3.2 Å or less, yet the average radius of aluminum ion in translational motion is estimated to be 4.7 Å from the diffusion coefficient,⁷ and in rotational motion it is estimated to be 5.0 Å from proton magnetic relaxation data reported in this paper.⁸ We may assume, therefore, that the mean time a water molecule remains adjacent to an $\text{Al}(\text{OH}_2)_6^{3+}$ ion is longer than the relaxation time for translation or rotation, and therefore longer than about 10^{-10} sec at 25°.

We now report a kinetic study of proton exchange between $\text{Al}(\text{OH}_2)_6^{3+}$ ions and solvent water molecules in dilute aqueous solution. Such a study can help to characterize the solvation of aluminum ion because a proton on its way from an $\text{Al}(\text{OH}_2)_6^{3+}$ site to an H_2O site in the bulk solvent necessarily passes through the solvation shell, and the mechanism of this process is bound to be instructive. In the present work, rates of proton exchange were measured at dynamic equilibrium by the nmr method. Our results confirm and extend recent kinetic studies of fast reactions of aqueous $\text{Al}(\text{OH}_2)_6^{3+}$ ion by the dissociation-field method,⁹ and of proton exchange rates at high concentrations of AlCl_3 by the nmr method.⁴

Acidity and Association of Aluminum Ion in Aqueous Acid

Before presenting our results, we wish to discuss the ionic species that might be present in solution. Our kinetic work was done in the pH range 3.3–0.5, well below that in which aluminum ion forms a hydrous gel. Under these conditions the formation of large complex ions, such as $\text{Al}[\text{Al}(\text{OH})_3]_n^{3+}$ or $\text{Al}[\text{Al}_2(\text{OH})_5]_n^{3+n}$, which is important above pH 4,¹⁰ can be shown to be negligible. The dominant reaction is acid dissociation of the aquo ion, as described by Brønsted and Volqvartz¹¹ and confirmed by others,^{7,12} including ourselves.¹³



Indeed, at low aluminum concentrations ($<0.01 M$) and pH (<4), reaction 1 is entirely sufficient, provided that allowance is made for ionic activity coefficients.

In estimating molar activity coefficients, γ , we have used the theory of Debye and Hückel in the form of

$$\log \gamma_z = -S z^2 \sqrt{\mu} / (1 + A \bar{a} \sqrt{\mu}) \quad (2)$$

In this equation, z is the charge number of the ion, μ the ionic strength of the solution, S the limiting slope (0.5114 in water at 30°), A a known parameter (0.3298 in water at 30°), and \bar{a} the "distance of closest approach" of the ions. We have used the single value of 6 Å for \bar{a} for all ions, which gives best fit to data on acid dissociation of 0.01–

(7) C. R. Frink and M. Peech, *Inorg. Chem.*, **2**, 473 (1963). These authors report the equivalent conductance of Al^{3+} at 25°; we have calculated the diffusion coefficient from their data.

(8) For a general reference, see J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, Chapter 9.

(9) L. P. Holmes, D. L. Cole, and E. M. Eyring, *J. Phys. Chem.*, **72**, 301 (1968).

(10) C. Brosset, *Acta Chem. Scand.*, **6**, 910 (1952); C. Brosset, G. Biedermann, and L. G. Sillén, *ibid.*, **8**, 1917 (1954).

(11) J. N. Brønsted and K. Volqvartz, *Z. Physik. Chem.*, **134**, 97 (1928).

(12) R. K. Schofield and A. W. Taylor, *J. Chem. Soc.*, 4445 (1954).

(13) E. Grunwald and D.-W. Fong, *J. Phys. Chem.*, **73**, 650 (1969).

0.05 M $(\text{H}_3\text{N})_5\text{CoOH}_2^{3+}$ in water¹¹ and is comparable to \bar{a} values reported for other trivalent metal chlorides.¹⁴

Between pH 3 and 4 and at aluminum concentrations above 0.01 M , reaction 1 in conjunction with (2) is no longer sufficient. To fit the thermodynamic data¹³ one must assume that the formation of hydrous Al_2O^{4+} becomes significant.



However, even at the highest aluminum concentration and pH employed in our kinetic work, reaction 3 will convert at most a few per cent of the total aluminum to hydrous Al_2O^{4+} . The formation of the conjugate acid, $\text{Al}_2\text{OH}^{5+} \cdot \text{aq}$, does not appear to be important under the conditions described in this work.

In the kinetic analysis we shall use the following thermodynamic data. For reaction 1, $K_A^\circ = 2.43 \times 10^{-5} M$ at 30° and $\Delta H^\circ \approx 11.5 \text{ kcal}$,^{12,13} for reaction 3, $K_3^\circ = 60 (M^{-1})$ at 30°; and molar activity coefficients are estimated by means of eq 2.

Interpretation of Nmr Data

Rates of proton exchange were deduced from precise spin-echo nmr measurements at 56.4 MHz of proton relaxation times T_1 and T_2 ¹⁵ in aqueous solutions containing 0.01–0.06 volume formal (vF) AlCl_3 and up to 0.3 vF HCl . Measurements were made in H_2O , and also in D_2O containing approximately 6 atom % of H.

In interpreting the nmr data in H_2O , we assume that proton exchange occurs between the OH sites in $\text{Al}(\text{OH}_2)_6^{3+}$ and those in bulk water. The fraction, p , of OH sites in $\text{Al}(\text{OH}_2)_6^{3+}$ is given by

$$p = 12[\text{Al}^{3+}] / (2[\text{water}] + 12[\text{Al}^{3+}]) \quad (4)$$

The proton chemical shift difference between the two sites is denoted by δ and will be expressed in radians/sec. Since p is small ($<10^{-2}$), there is under all conditions only one intense or *dominant*¹⁶ OH-proton resonance, even when exchange is slow and the two OH resonances are not averaged by the exchange. T_1 and T_2 are measured for this dominant resonance. The exchange broadening,¹⁵ $(1/T_2) - (1/T_1)$, is related to the proton exchange rate r_E as in (5), which involves a parameter, τ , defined in (6).¹⁵

$$(1/T_2) - (1/T_1) = p\delta^2\tau / (1 + \delta^2\tau^2) \quad (5)$$

$$\tau^{-1} = r_E / 12[\text{Al}^{3+}](1 - p) \quad (6)$$

Equation 5 is quadratic in τ and has two roots. To find the physically correct one, we measured $(1/T_2) - (1/T_1)$ as a function of temperature; examples are shown in Figure 1. The curve goes through a maximum at the temperature at which $\tau^{-1} = \delta$. Above this temperature we select the root that is greater than δ ; below this temperature we select the root that is smaller than δ . The magnitude of the maximum evaluates δ , since $[(1/T_2) - (1/T_1)]_{\text{max}} = p\delta/2$.

Proton exchange rates in a nominal D_2O solvent containing a small fraction of protons are measured analogously. After establishment of isotopic equilibrium, the nominal substrate is $\text{Al}(\text{OD}_2)_6^{3+}$ and likewise contains only a small fraction of protons. In principle the distribu-

(14) F. H. Spedding, P. E. Porter, and J. M. Wright, *J. Amer. Chem. Soc.*, **74**, 2781 (1952).

(15) See, for example, E. Grunwald and M. S. Puar, *J. Phys. Chem.*, **71**, 1842 (1967).

(16) S. Meiboom, *J. Chem. Phys.*, **34**, 387 (1961).

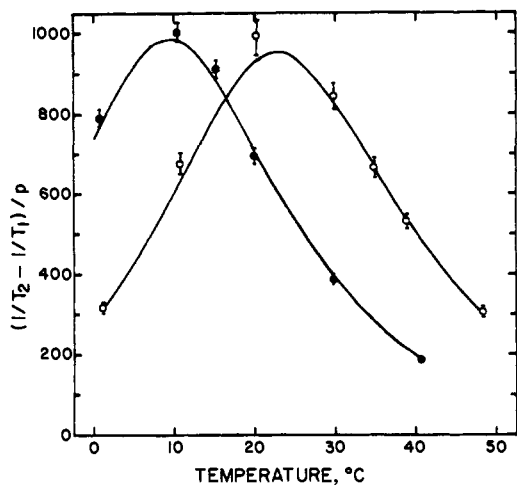


Figure 1. Exchange broadening, $[(1/T_2) - (1/T_1)]/p$, vs. temperature: ●, 0.040 M AlCl_3 and 0.049 M HCl in H_2O ; ○, 0.058 M AlCl_3 and 0.058 M HCl in $\text{HOD-D}_2\text{O}$ with $f = 0.06$. Solid curves are calculated, respectively, from eq 5 and 18 with $\delta = 1960 \text{ sec}^{-1}$, and from eq 5 and 17 with $\delta = 1900 \text{ sec}^{-1}$. Details are given in the Experimental Part.

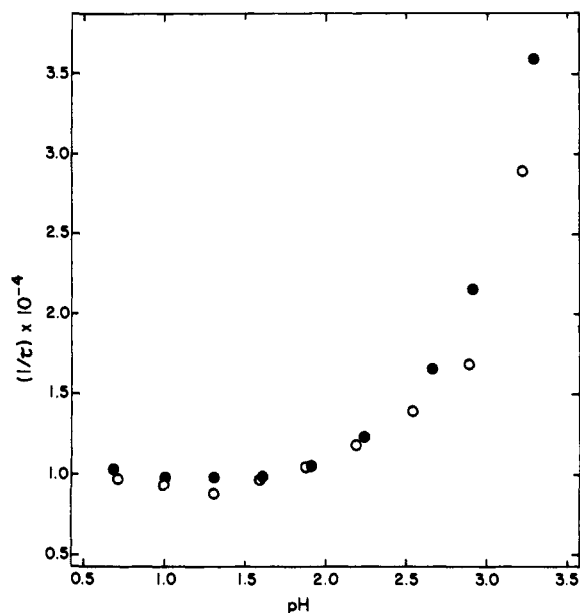


Figure 2. $1/\tau$ vs. pH in H_2O at 29.9° : ●, 0.059 M AlCl_3 and HCl; ○, 0.020 M AlCl_3 and HCl.

tion of protons among the two sites is not quite statistical, but our nmr measurements show that the isotopic fractionation factor is within experimental error ($\pm 10\%$) of unity. We have assumed, therefore, that the distribution is statistical. If f denotes the proton fraction, $[\text{H}]/([\text{H}] + [\text{D}])$, in the solution, then rates may be calculated from eq 4, 5, and 6'.

$$\tau^{-1} = r_E/12f[\text{Al}^{3+}](1-p) \quad (\text{D}_2\text{O}) \quad (6')$$

Rates of Exchange

The pH dependence of τ^{-1} is illustrated in Figure 2 for two different aluminum concentrations. It is seen that τ^{-1} is quite independent of pH at low pH; we shall show

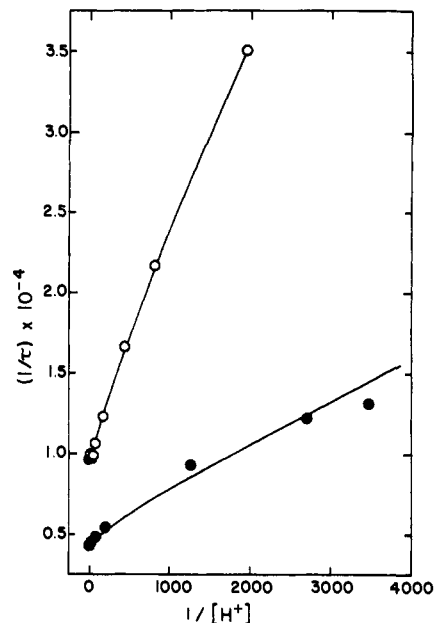


Figure 3. $1/\tau$ vs. $1/[\text{H}^+]$: ○, 0.059 M AlCl_3 in H_2O at 29.9° ; ●, ~ 0.02 M AlCl_3 in $\text{HOD-D}_2\text{O}$ at 34.5° (actual AlCl_3 concentrations range from 0.019 to 0.024 M; smooth curve calculated for 0.02 M). Smooth curves are calculated on the basis of eq 28 and 33 and data in Table IV. AlCl_3 and a trace of HCl (to produce the desired pH) are the only electrolytes.

that the small variation below pH 1 is probably a kinetic salt effect. However, above pH 2 the rate increases markedly with pH, even though the ionic strength is now virtually constant. Figure 3 shows some typical plots of τ^{-1} vs. $[\text{H}^+]^{-1}$ under otherwise constant conditions. The plots show mild downward curvature, especially when $[\text{H}^+]^{-1} > 500$. Our results are collected in Tables I and II.

Identification of Rate Processes

As a first step, we shall consider only the data up to $[\text{H}^+]^{-1} \approx 500$. According to Figure 3, at constant $[\text{Al}^{3+}]$ and ionic strength these data can be fitted with fair accuracy to a linear rate law (eq 7), where j_2 and j_1 denote the slope and intercept, respectively. We use the symbols

$$\frac{12}{\tau} = \frac{r_E}{[\text{Al}^{3+}]} = j_1 + j_2/[\text{H}^+] \quad (7)$$

j_2 and j_1 rather than the conventional k 's of rate laws to emphasize that slope and intercept may still be functions of aluminum concentration.

Results are given in Table III. Both specific rates j_1 and $j_2/[\text{H}^+]$ are substantially greater than the known rate of exchange of oxygen atoms between $\text{Al}(\text{OH}_2)_6^{3+}$ and bulk water.^{3,6} Thus all but a very small fraction of the proton exchange measured in our experiments results from protolysis rather than from the exchange of whole water molecules. Since j_1 is quite constant, we may identify it with the rate constant for a first-order reaction of $\text{Al}(\text{OH}_2)_6^{3+}$, and there is little doubt that that reaction is acid dissociation, that is $j_1 = k_a$ in eq 1. The kinetics of acid dissociation was studied recently by the dissociation field method, and k_a was found to be $1.09 \times 10^5 \text{ sec}^{-1}$ at 25° .⁹ Our value for j_1 , corrected to 25° on the basis of

Table I. Kinetic Results in H₂O at 29.9°

p _c H ^a	10 ⁻³ /τ, sec ⁻¹		p _c H ^a	10 ⁻³ /τ, sec ⁻¹	
	Obsd	Calcd ^b		Obsd	Calcd ^b
	[AlCl ₃] = 0.059 M			[AlCl ₃] = 0.020 M	
0.706	10.4	...	0.708	9.77	...
1.005	9.83	...	1.009	9.47	...
1.303	9.85	9.55	1.310	8.77	9.41
1.600	9.95	10.04	1.583	9.77	9.68
1.914	10.7	10.96	1.889	10.5	10.24
2.233	12.4	12.56	2.194	11.8	11.27
2.652	16.7	16.60	2.529	14.0	13.45
2.910	21.7	21.30	2.886	16.8	18.34
3.291	35.1	35.16	3.226	29.0	28.45
	[AlCl ₃] = 0.040 M			[AlCl ₃] = 0.010 M	
0.524	11.0	...	0.521	10.4	...
0.708	10.2	...	0.706	9.88	...
1.009	9.35	...	1.007	9.42	...
1.310	9.58	9.57	1.325	9.55	9.17
1.602	9.53	9.93	1.620	10.1	9.40
1.921	10.8	10.66	1.947	9.79	9.90
2.222	11.5	11.89	2.220	10.7	10.70
2.553	15.0	14.32	2.529	12.8	12.42
2.854	18.9	18.44	2.857	14.9	16.12
3.318	33.3	33.26	3.128	27.1	22.12
	[AlCl ₃] = 0.030 M, [NaCl] = 0.18 M				
1.293	10.5	10.46			
1.587	10.6	10.73			
1.894	11.5	11.27			
2.210	11.8	12.27			
2.603	14.7	14.80			
2.999	21.7	20.46			
3.384	32.8	33.26			

^ap_cH = -log [H⁺], where [H⁺] is the molar concentration of hydrogen ion. ^bEquation 28 and data in Table IV.

Table II. Kinetic Results at 34.5° in HOD-D₂O Containing Ca. 6 Atom % of H

p _c H ^a	10 ⁻³ /τ, sec ⁻¹		p _c H ^a	10 ⁻³ /τ, sec ⁻¹	
	Obsd	Calcd ^b		Obsd	Calcd ^b
	[AlCl ₃] = 0.059 M			[AlCl ₃] = 0.021 M	
1.301	4.63	4.53	1.299	4.47	4.58
1.374	4.65	4.56	1.410	4.52	4.61
1.565	4.44	4.65	1.979	4.90	4.89
1.854	4.87	4.88	2.309	5.48	5.31
2.230	5.52	5.43	3.109	9.27	8.50
2.408	5.82	5.86	3.434	12.4	12.23
			3.544	13.3	14.26
			3.742	(16.8) ^c	...

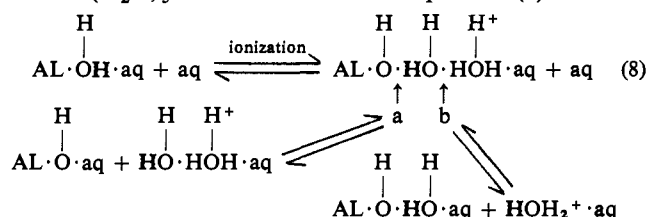
^ap_cH = -log [H⁺], where [H⁺] is the molar concentration of hydrogen ion. ^bEquation 33 and data in Table IV. ^cRelatively poor accuracy. Omitted from curve fitting.

data reported later (eq 18), is $0.79 \times 10^5 \text{ sec}^{-1}$. Actually, k_a as measured by the dissociation field method is not quite comparable with our value because the relaxation takes place in a strong electric field.

A kinetic term of the form $j_2/[H^+]$ might arise from the reaction of $\text{Al}(\text{OH})_2^{3+}$ with OH^- . However, this theory must be rejected because the maximum specific rate for such a process, assuming reaction at each encounter, is less than 0.01% of $j_2/[H^+]$. Thus $j_2/[H^+]$ must be identified with a reaction of, or involving, the conjugate base of the hydrated aluminum ion.

Site of Dissociation in Acid Dissociation. The rate constant, k_{-a} , for the reaction of hydrogen ion with $(\text{H}_2\text{O})_5\text{AlOH}^{2+}$ (eq 1) is of the correct magnitude (Table III) for a diffusion-controlled reaction mechanism.⁹ It is

fruitful, therefore, to represent acid dissociation as involving two consecutive reaction steps, ionization and dissociation. A possible and convenient mechanism for further discussion is shown schematically in (8), where $\text{AL} \equiv (\text{H}_2\text{O})_5\text{Al}$. The ionized complex in (8) can dis-



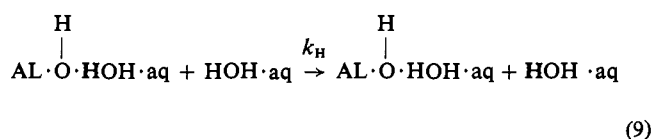
sociate either at site a, adjacent to $\text{AL}(\text{OH})$, or at a site that is farther removed, such as b. In case a, the O·HO

Table III. Preliminary Kinetic Analysis on the Basis of Eq 7^a

[AlCl ₃], <i>M</i>	[NaCl], <i>M</i>	<i>j</i> ₁ = <i>k</i> _a	<i>j</i> ₂	<i>K</i> _A	<i>k</i> _{-a}	<i>j</i> ₂ / <i>K</i> _A
0.0100	...	1.07 ₁ × 10 ⁵	169	1.12 × 10 ⁻⁵	0.96 × 10 ¹⁰	1.51 × 10 ⁷
0.0201	...	1.08 ₇ × 10 ⁵	158	0.92 ₁ × 10 ⁻⁵	1.18 × 10 ¹⁰	1.72 × 10 ⁷
0.0301	0.18	1.22 ₅ × 10 ⁵	132	0.66 ₄ × 10 ⁻⁵	1.84 × 10 ¹⁰	1.99 × 10 ⁷
0.0401	...	1.10 ₃ × 10 ⁵	167	0.75 ₃ × 10 ⁻⁵	1.47 × 10 ¹⁰	2.21 × 10 ⁷
0.0587	...	1.08 ₀ × 10 ⁵	192	0.67 ₃ × 10 ⁻⁵	1.61 × 10 ¹⁰	2.86 × 10 ⁷

^a Measurements in H₂O at 29.9°.

hydrogen bond breaks whenever the ionized complex dissociates; in case b it remains intact. In order for the reversible cycle of acid dissociation to lead to proton exchange in case b, the O·HO hydrogen bond must break in a subsequent process, *before* the AL(OH)·HOH ion reacts with hydrogen ion and AL(OHH) is re-formed. Possible processes by which the hydrogen bond might break have been discussed in another connection.¹⁷ An example, exchange of a water molecule between site a and the bulk solvent, is shown in eq 9.



The rate law for proton exchange will depend on the site of dissociation, as shown in eq 10. In (10b), *k*_H is the rate

Case a

$$r_{\text{E}} = k_{\text{a}}[\text{AL} \cdot \text{OH}_2] \quad (10a)$$

Case b

$$r_{\text{E}} = k_{\text{a}}[\text{AL} \cdot \text{OH}_2] \cdot k_{\text{H}} / (k_{\text{H}} + k_{-\text{a}}[\text{H}^+]) \quad (10b)$$

constant for breaking the O·HO hydrogen bond in the AL(OH)·HOH ion, and *k*_H/(*k*_H + *k*_{-a}[H⁺]) is the probability that the hydrogen bond will break before the ion reacts with hydrogen ion.

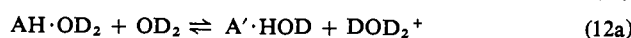
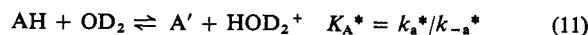
According to data cited in the introductory section, *k*_H for reaction 9 should be less than about 10¹⁰ sec⁻¹. (We shall see that the actual value is close to 4 × 10⁷ sec⁻¹.) According to Table III, *k*_{-a} ≈ 1.5 × 10¹⁰ sec⁻¹ M⁻¹. Thus in case b, *k*_H/(*k*_H + *k*_{-a}[H⁺]) should be clearly less than 1.0 when [H⁺] > 0.1 M. Our rate measurements extend up to 0.3 M HCl without any sign that the first-order rate is decreasing. Case a is therefore experimentally correct.

We were surprised by this result. There is little doubt that the tightly solvated aluminum ion is a strongly "order producing" ion in water.¹⁸ Why then should acid dissociation take place by such a mechanism that the ordered solvation shell is disrupted severely? We thought we had better prove this result by an independent method.

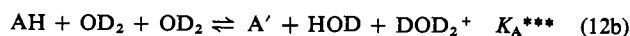
The method we decided to try consisted of measuring proton exchange in a solvent composed largely of D₂O. This method can be instructive, because acid dissociation of a proton acid HA in D₂O can result in the formation of HOD₂⁺ (eq 11) or D₃O⁺ (eq 12), depending on the mechanism.

(17) E. Grunwald and E. K. Ralph, *J. Amer. Chem. Soc.*, **89**, 4405 (1967).

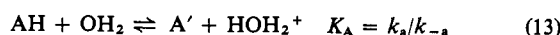
(18) R. W. Gurney, "Ionic Processes in Solution," McGraw-Hill Book Co., Inc., New York, N. Y., 1953.



$$K_{\text{A}}^{**} = k_{\text{a}}^{**}/k_{-\text{a}}^{**}$$



If the reverse reaction is diffusion controlled, the solvent isotope effect on *k*_a can be predicted by means of the Gross-Butler theory^{19-21a} and is distinctly different for (11) and (12). For definiteness, consider (11) and the analogous process (13) in H₂O. On making the usual



assumptions of the theory,¹⁹ we find from (11) and (13) that

$$\frac{K_{\text{A}}^*}{K_{\text{A}}} = \frac{(\text{HOD}_2^+)(\text{OH}_2)}{(\text{OD}_2)(\text{H}_3\text{O}^+)} = \frac{k_{\text{OD}_2}^{+\text{H}}}{k_{\text{OH}_2}^{+\text{H}}} = 3L^{-1/3} \quad (14)$$

where *k*_{OD₂⁺H = (HOD₂⁺)/(H⁺)(D₂O), *k*_{OH₂⁺H = (H₃O⁺)/(H⁺)(H₂O), and *L* = (H₃O⁺)²(OD₂)³/(D₃O⁺)²(H₂O)³ = 10.4 at 30°. Furthermore, *K*_A^{*}/*K*_A = (*k*_a^{*}/*k*_a) · (*k*_{-a}/*k*_{-a}^{*}). If the reverse reaction is diffusion controlled, we may write *k*_{-a} = *k*_e*P* and *k*_{-a}^{*} = *k*_e^{*}*P*^{*}, where *k*_e(*k*_e^{*}) is the rate constant for the formation of encounter complexes and *P*(*P*^{*}) is the probability that an encounter results in proton transfer. Next we approximate *k*_e^{*}/*k*_e by the relative viscosity η_{H₂O}/η_{D₂O}, and *P*^{*}/*P* by 1/3, the statistical probability that A' is adjacent to H in the encounter complex A'·(OHD₂⁺). The result is}}

$$\frac{k_{\text{a}}^*}{k_{\text{a}}} = \frac{K_{\text{A}}^*}{K_{\text{A}}} \frac{k_{-\text{a}}^*}{k_{-\text{a}}} = 3L^{-1/3} (\eta_{\text{H}_2\text{O}}/3\eta_{\text{D}_2\text{O}}) \quad (15a)$$

$$= 0.37 \text{ at } 30^\circ \quad (15b)$$

By an analogous method it can be predicted that when the product is D₃O⁺, the solvent isotope effect is (16).

$$k_{\text{a}}^{**}/k_{\text{a}} = k_{\text{a}}^{***}/k_{\text{a}} = \eta_{\text{H}_2\text{O}} L^{-1/2} / \eta_{\text{D}_2\text{O}} \quad (16a)$$

$$= 0.25 \text{ at } 30^\circ \quad (16b)$$

For hexahydratoaluminum ion it is convenient to compare 1/τ in H₂O and D₂O, since that is the specific rate of exchange per OH bond. Results shown in Figure 1 are represented by the following Arrhenius equations. For 0.058 M AlCl₃ and 0.058 M HCl in HOD-D₂O with *f* = 0.06

$$-\log \tau_{\text{D}_2\text{O}} = 13.062 - 2894/T \quad (17)$$

(19) E. L. Purlee, *J. Amer. Chem. Soc.*, **81**, 263 (1959).

(20) P. Salomaa, L. L. Schaleger, and F. A. Long, *J. Phys. Chem.*, **68**, 410 (1964).

(21) (a) We are indebted to Dr. V. Gold for showing us how to derive the same result by an alternative method, and for helpful discussion. (b) If we abandon the assumption that there is no isotopic fractionation, the "best value" is 0.37 ± 0.02.

For 0.040 M AlCl₃ and 0.049 M HCl in H₂O

$$-\log \tau_{\text{H}_2\text{O}} = 13.369 - 2845/T \quad (18)$$

Equation 17 fits with a correlation coefficient of 0.9993 and a standard error in log τ of 0.013; the value derived for the activation energy is 13.24 ± 0.13 kcal. Equation 18 fits with a correlation coefficient of 0.9979 and a standard error of 0.021 log unit; the activation energy is 13.02 ± 0.27 kcal.

On subtracting (18) from (17), we obtain (19), for which the standard error of fit is 0.025 log unit. Hence $\tau_{\text{H}_2\text{O}}/\tau_{\text{D}_2\text{O}}$

$$\log \tau_{\text{H}_2\text{O}}/\tau_{\text{D}_2\text{O}} = -0.307 - 49/T \quad (19)$$

$\tau_{\text{D}_2\text{O}} = 0.34 \pm 0.02$ at 30°, in reasonable agreement^{21b} with prediction for a mechanism leading to HOD₂⁺, but not for one leading to D₃O⁺. It follows that the ionized state that dissociates in H₂O must be formulated as AL(OH)·HOH₂⁺, and that dissociation takes place at site a.

If this result be accepted, then it follows from microscopic reversibility that the reverse process, namely the reaction of hydrogen ion with the hydrated AL(OH) ion, also proceeds by a mechanism in which the hydrogen bond at site a breaks. We shall have to make use of this finding in a later section, in order to fit the kinetic results for proton exchange at higher pH.

The Sign of the Salt Effect on k_a . Available evidence suggests that the sign of the salt effect may be another criterion for mechanism. In the acid dissociation of alkyl-substituted ammonium and pyridinium NH⁺ acids in water, dissociation takes place at site b and addition of electrolyte reduces k_a .^{17, 22} In the present case, on the other hand, addition of HCl and NaCl, and perhaps also of AlCl₃ at high concentration, results in an increased rate of proton exchange. For HCl, at the moderate concentrations used, the increase is roughly linear (data in Table I) and can be represented by eq 20, where the coefficient $B_{\text{HCl}} = (0.65 \pm 0.14) \times 10^5 \text{ sec}^{-1} M^{-1}$ at 30°.

$$r_E/[Al^{3+}] = j_1 + B_{\text{HCl}}[\text{HCl}] \quad (20)$$

To test whether this rate increase results from a new reaction, in which H₃O⁺ is an acid catalyst,²³ or from a salt effect on k_a , we did a series of measurements in the presence of 0.18 M NaCl and found the first-order rate constant to increase also (Table III). Assuming the increase to be linear with [NaCl], the coefficient B_{NaCl} (analogous to B_{HCl}) was evaluated as $0.7 \times 10^5 \text{ sec}^{-1} M^{-1}$ at 30°, virtually identical with B_{HCl} .

Regarding the salt effect of AlCl₃, our own data at low concentrations (Table III) show no clear trend. However, Takahashi,^{4b} extrapolating from data at much lower temperatures, has reported a first-order rate constant for 1.59 M AlCl₃ at 25° that is distinctly larger than our j_1 , thus providing preliminary evidence for a positive salt effect.

One can make quite a plausible argument that the salt

(22) (a) M. T. Emerson, E. Grunwald, and R. A. Kromhout, *J. Chem. Phys.*, **33**, 547 (1960); (b) E. Grunwald, *J. Phys. Chem.*, **67**, 2211 (1963); (c) M. Cocivera, *ibid.*, **72**, 2520 (1968).

(23) T. A. Stephenson, T. J. Swift, and J. B. Spencer, *J. Amer. Chem. Soc.*, **90**, 4291 (1968), find that proton exchange between various aquated cation species and water is formally general acid-catalyzed, with formal rate constants on the order of $10^5 \text{ sec}^{-1} M^{-1}$ at 25° in most cases. However, the Brønsted catalysis law is not obeyed, and in some cases H₃O⁺ is a less effective "catalyst" than much weaker carboxylic acids.

effect on k_a should be negative when dissociation takes place at site b and positive when it takes place at site a. The added ions will bind some water molecules tightly and remove others from the normal liquid lattice of water without binding them directly.²⁴ These interactions should increase the amount of work needed to align water molecules so as to permit proton conduction beyond site b, but the increased "disorder" they produce should facilitate the departure of the H₃O⁺ ion from site a without proton transfer.

Reaction of AL·OH

It has been pointed out that the increase in r_E at the higher pH must be assigned to a proton-transfer reaction involving AL·OH. We now wish to characterize this reaction by kinetic analysis. In that analysis, AL·OH will be treated as a reactive intermediate of low concentration.

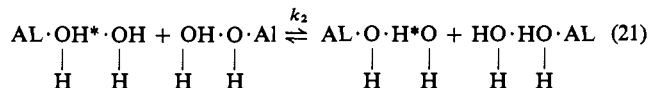
Let us begin by examining the parameter j_2 in the approximate rate law, eq 7. If AL·OH is a reactant, then

$$r_E/[AL \cdot OH] = r_E[H^+]/K_A[AL \cdot OH_2] = j_2/K_A$$

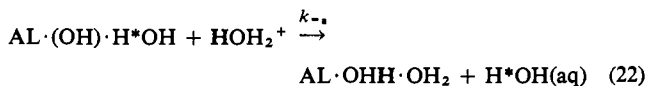
Values of j_2/K_A are listed in Table III and increase regularly with the aluminum concentration, showing that at least part of the proton exchange results from a reaction of AL·OH with AL·OH₂.

In searching for the complete rate law, we have considered a number of reaction mechanisms and compared their kinetic consequences with the experimental data. To be acceptable, a reaction mechanism must reproduce the curvature illustrated in Figure 3, accommodate the observed D₂O solvent isotope effect, be compatible with the established mechanism of acid dissociation, and lead to plausible rate constants. We shall state at once that these constraints proved to be severe; after testing numerous models, we found only one that seemed to fit the facts without major difficulty and without involving more than three parameters.

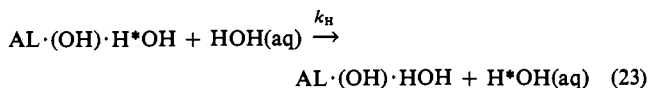
Suppose that the only proton-transfer reaction taking place in addition to acid dissociation is that of AL·OH₂ with AL·OH, and that that reaction involves at least two additional water molecules. In view of the strong solvation of these ions, we may represent such a process as a bimolecular reaction of the hydrated ions, as in



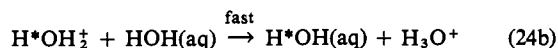
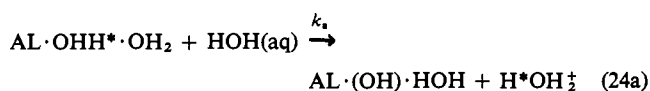
Since we are measuring proton exchange between AL·OH₂ and water molecules in the bulk solvent, reaction 21 can be detected only if the proton denoted by H* ends up on a water molecule in the bulk solvent. Thus, if the short-lived AL·(OH)·H*OH reverts to AL·(OHH*)·OH₂ by undergoing reaction 21 in reverse, there is no proton exchange. But if it reacts with H₃O⁺ by a mechanism that is the microscopic reverse of acid dissociation (eq 22), or if the hydrated complex dissociates (eq 23) before the AL·OH ion reacts by either process, there is proton exchange.



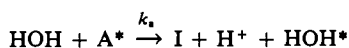
(24) See, for example, G. H. Haggis, J. B. Hasted, and T. J. Buchanan, *J. Chem. Phys.*, **20**, 1452 (1952); H. S. Frank and W.-Y. Wen, *Discussions Faraday Soc.*, **24**, 133 (1957).



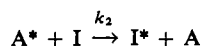
In order to derive the rate law for proton exchange, we must represent acid dissociation consistently as involving the hydrated ions, as in



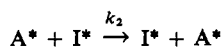
Inspection of (21)–(24) then shows that there are two reactive intermediates, I^* and I , where $I^* \equiv \text{AL}\cdot(\text{OH})\cdot\text{H}^*\text{OH}$ and $I \equiv \text{AL}\cdot(\text{OH})\cdot\text{HOH}$. We shall represent proton exchange by $A^* + \text{HOH} \rightarrow A + \text{HOH}^*$, where $A^* \equiv \text{AL}\cdot\text{OHH}^*\cdot\text{OH}_2$ and $A \equiv \text{AL}\cdot\text{OH}_2\cdot\text{OH}_2$. Individual reactions are then shown as follows. Acid dissociation



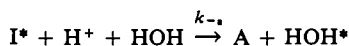
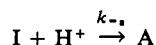
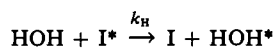
Reaction 21



Reaction 23



Reaction 22



We shall further introduce two variables, g and h , which are defined in (25) and (26). g is the probability that the

$$g = k_2[\text{Al}^{3+}]/(k_{-a}[\text{H}^+] + k_2[\text{Al}^{3+}]) \quad (25)$$

$$h = k_H/(k_{-a}[\text{H}^+] + k_2[\text{Al}^{3+}] + k_H) \quad (26)$$

reactive intermediate (I^* or I) reacts according to (21) rather than according to (22). h is the probability that I^* is converted to I .

The kinetic scheme for proton exchange is then shown in Figure 4. (Water molecules are omitted for the sake of clarity.) The scheme is formally analogous to that for a radical chain reaction. Acid dissociation is analogous to chain initiation, in which a reactive intermediate is produced; reaction 21 is analogous to chain propagation, in which one reactive intermediate disappears and a new one is formed; and reaction 22 is analogous to chain termination, in which the reactive intermediate is destroyed. The rate law can be derived by making the usual steady-state approximations, or more intuitively, by inspection of Figure 4, as the sum of an infinite series of probability factors, as follows.

$$\frac{dA}{dt} = r_E = k_a[\text{Al}^{3+}]\{(1-g) + g + g(1-g) + g^2h + g^2(1-g) + g^3h + g^3(1-g) + g^4h + \dots\}$$

In this representation, $k_a[\text{Al}^{3+}]$ is the rate of "chain initiation"; the terms proportional to $(1-g)$ give proton exchange resulting from "chain termination"; and the

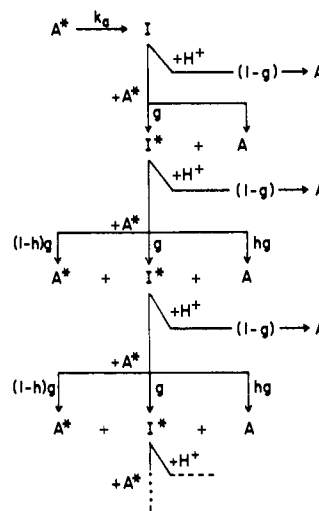


Figure 4. Kinetic scheme for proton exchange.

other terms give proton exchange resulting from "chain propagation." Since $1 + g + g^2 + \dots = (1-g)^{-1}$, the series can be written simply in closed form, as in (27).

$$r_E = k_a[\text{Al}^{3+}]\{1 + g + [g^2h/(1-g)]\} \quad (27)$$

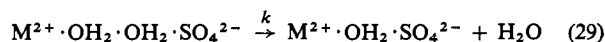
Equation 27 is qualitatively of the correct form to be consistent with our data. At low pH, g approaches zero; hence $r_E/[\text{Al}^{3+}]$ approaches k_a , as it should. To obtain the rate law at higher pH, we express g and h in terms of rate constants (eq 25 and 26), substitute in (27), and recall that $k_a/k_{-a} = K_A$. The result is

$$r_E = k_a[\text{Al}^{3+}] + \frac{k_2K_A[\text{Al}^{3+}]^2}{[\text{H}^+]} \times \left(1 - \frac{k_2[\text{Al}^{3+}]}{k_{-a}[\text{H}^+] + k_2[\text{Al}^{3+}] + k_H}\right) \quad (28)$$

Equation 28 predicts that the plot of $r_E/[\text{Al}^{3+}]$ vs. $1/[\text{H}^+]$ has downward curvature, as observed. The slope ranges from $k_2K_A[\text{Al}^{3+}]$ when $k_{-a}[\text{H}^+] \gg k_2[\text{Al}^{3+}]$ to $k_2K_A[\text{Al}^{3+}]k_H/(k_2[\text{Al}^{3+}] + k_H)$ when $[\text{H}^+]$ is very small.

The fit of eq 28 is satisfactory. Values of k_a , k_H , and k_2 were evaluated for each series of experiments and are shown in Table IV. Values of $1/\tau$ calculated with these rate constants are compared with the experimental data in Table I. Agreement with experiment is always within the experimental error, which increases with decreasing concentration of AlCl_3 .

Values obtained for the rate constants are plausible. k_a is almost exactly the same as its preliminary counterpart j_1 (Table III) and need not be discussed again. k_H for $\text{AL}(\text{OH})_2^+ \cdot \text{HOH}$ is about $4 \times 10^7 \text{ sec}^{-1}$ at 30° . As far as we know, this is the first experimental estimate of the lifetime of an encounter complex between an aquated ion of charge +2 and a water molecule. It should be noted, however, that k_H is of the same magnitude as experimental estimates of the rate constant for a related process, the replacement of a water molecule by a sulfate ion on the site adjacent to a hydrated cation (eq 29).²⁵



(25) G. Atkinson and S. K. Kor, *J. Phys. Chem.*, **69**, 128 (1965); G. Atkinson and S. Petrucci, *ibid.*, **70**, 3122 (1966).

Table IV. Kinetic Analysis on the Basis of Eq 28 and 33

[AlCl ₃], M	k_a, k_a^* , sec ⁻¹ × 10 ⁻⁵	k_{-a}, k_{-a}^* , sec ⁻¹ M ⁻¹ × 10 ⁻¹⁰	k_H, k_H^* , sec ⁻¹ × 10 ⁻⁷	k_2, k_2^* , sec ⁻¹ M ⁻¹ × 10 ⁻⁸
Measurements at 29.9° in H ₂ O ^a				
0.0100	1.07	0.96	~5.0	13
0.0201	1.09	1.18	4.2	10.7
0.0301 ^b	1.22	1.84	3.7	9.3
0.0401	1.10	1.47	3.5	8.3
0.0587	1.08	1.61	3.6	8.9
Measurements at 34.5° in HOD-D ₂ O ^c				
0.0209 ^d	0.54	(1.01) ^e	(3.0) ^e	5.9
0.0585 ^e	0.53	(1.37) ^e	(3.0) ^e	5.6

^aEquation 28; required values of K_A are listed in Table III. ^b0.18 M NaCl added to the solutions used in this series. ^cEquation 33; $k_{-a}^* = k_{-a}\eta_{H_2O}/\eta_{D_2O}$; $k_H^* = k_H\eta_{H_2O}/\eta_{D_2O}$. ^d $10^6 K_A^{D_2O} = 3.98$. ^e $10^6 K_A^{D_2O} = 2.93$.

Values of the rate constant k in (29) are $7 \times 10^7 \text{ sec}^{-1}$ when $M = \text{Mg}$ or Mn .²⁵

The high value obtained for k_2 , $9 \times 10^8 \text{ sec}^{-1} \text{ M}^{-1}$ in water at 29.9°, suggests that electrostatic repulsion between the ionic reactants, which are of like charge, is relatively unimportant. The high value is consistent with a transition-state model for the reaction in which the ionic charges are quite far apart and hence supports the theory that two or more water molecules participate, as suggested in (21). Apparently, when solvation of the ionic reactants is strong and a suitable hydrogen-bonded pathway exists, proton transfer can take place rapidly along a chain of several water molecules, as in ice,²⁶ in spite of the macroscopic fluidity of the liquid medium.

In a recent study of proton exchange in aqueous phosphate buffers, Luz and Meiboom²⁷ found a dominant process involving H_2PO_4^- , HPO_4^{2-} , and one or more H_2O molecules. In spite of the like charges of the ionic reactants, the rate constant for this process is also very high, and it is consistent with a diffusion-controlled proton transfer involving two or more water molecules.²⁷ The analogy goes even further. Values of k_2 in Table IV are surprisingly independent of the ionic strength of the solution. Luz and Meiboom found that their data, over a comparable range of ionic strength, are similarly represented by a constant second-order rate coefficient. One is tempted to speculate that when the distance between the charges in the transition state for the reaction is large, ion-atmosphere effects resemble those on the free reactant ions.

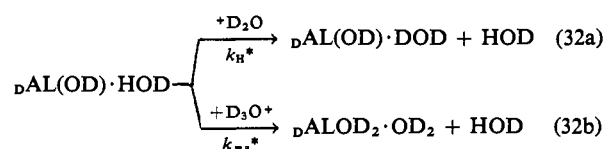
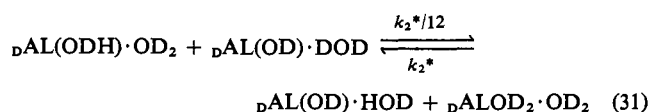
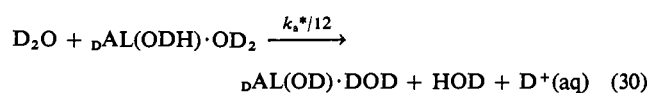
Kinetic Analysis for HOD-D₂O

We shall assume that the proton fraction, f , is very small, so that the relevant reactions are variants of (21)–(24) in which one hydrogen atom is H and all others are D. The rate of proton exchange is then calculated on the basis of the following scheme, in which ${}_D\text{AL} \equiv \text{Al}(\text{OD}_2)_5$.²⁸

(26) (a) M. Eigen and L. de Maeyer in "The Structure of Electrolytic Solutions," W. J. Hamer, Ed., John Wiley and Sons, Inc., New York, N. Y., 1959, Chapter 5. (b) This evidence, that proton conduction can take place in a fluid medium by the same mechanism as in ice, lends some support to current speculations that a similar "facilitated proton transfer" might be important in enzyme catalysis: J. H. Wang, *Science*, 161, 328 (1968).

(27) Z. Luz and S. Meiboom, *J. Amer. Chem. Soc.*, 86, 4764 (1964).

(28) If f is small rather than very small, ${}_D\text{AL}$ is a mixture of $\text{AlO}_5\text{D}_{10}$, $\text{AlO}_5\text{D}_9\text{H}$, etc.



The rate constant for acid dissociation in (30) is denoted by $k_a^*/12$, to make k_a^* directly comparable with k_a in H_2O where the aluminum ion is associated with 12 exchangeable protons. The rate constant for the forward reaction (31) is denoted by $k_2^*/12$ for a similar reason. Assuming that isotopic fractionation factors are unity, the equilibrium constant for (31) is found from the statistical factors (number of equivalent reactive sites) of reactants (1 and 1) and products (1 and 12) to be $1/12$,²⁹ hence the rate constant for the reverse reaction is denoted by k_2^* . The concentration of ${}_D\text{AL} \cdot \text{OD}_2 \cdot \text{OD}_2 \approx [\text{Al}^{3+}]$; that of ${}_D\text{AL}(\text{ODH}) \cdot \text{OD}_2 = 12f[\text{Al}^{3+}]$.

The scheme (30–32) contains two short-lived intermediates: ${}_D\text{AL}(\text{OD}) \cdot \text{DOD}$, whose concentration is $K_A^{D_2O}[\text{Al}^{3+}]/[\text{H}^+]$, and ${}_D\text{AL}(\text{OD}) \cdot \text{HOD}$. On making the steady-state approximation for the concentration of the latter, we obtain (33) for the rate of proton exchange.

$$r_E = k_a^* f [\text{Al}^{3+}] + \frac{k_2^* K_A^{D_2O} f [\text{Al}^{3+}] (k_H^* + k_{-a}^* [\text{D}^+])}{[\text{D}^+] (k_H^* + k_{-a}^* [\text{D}^+] + k_2^* [\text{Al}^{3+}])} \quad (33)$$

Note that (33) is formally identical with (28). There are some subtle differences, however. k_a^* is the specific rate of acid dissociation of the proton in ${}_D\text{AL}(\text{ODH})$, while $K_A^{D_2O}$ is the dissociation constant of the deuteron in ${}_D\text{AL}(\text{OD}_2)$. We shall assume, in keeping with our earlier discussion, that $K_A^{D_2O}/K_A^{H_2O} = L^{-1/2}$, or 0.318 at 34.5°. We shall further assume that $k_{-a}^*/k_{-a} = k_H^*/k_H = \eta_{H_2O}/\eta_{D_2O}$. Thus k_{-a}^* and k_H^* can be predicted. The re-

(29) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, pp 199–200.

Table V. OH-Proton T_1 in H_2O Solutions of $AlCl_3$ and 0.01 M HCl at 29.9°

$[AlCl_3], M$	$10^3 p$	$1/T_1, sec^{-1}$	η/η_0^a	$\eta_0/\eta T_1$
...	0.00	0.326 ± 0.005	1.005	0.324
0.0100	1.08	0.330 ± 0.003	1.013	0.326
0.0201	2.17	0.342 ± 0.003	1.021	0.335
0.0401	4.33	0.355 ± 0.006	1.035	0.343
0.0587	6.34	0.377 ± 0.002	1.047	0.360

^a η_0 = viscosity of pure water at 29.9°.

maining parameters, k_a^* and k_2^* , are then obtained by adjustment to the data.

The results of this treatment are summarized in Table IV, and the satisfactory fit of the data is shown in Table II. The fit is well within the experimental error, which is greater in HOD-D₂O than in H₂O. The solvent isotope effect on k_a has already been discussed. (Equations 17 and 18 describe conditions under which $12/\tau = k_a$ or k_a^* .) The solvent isotope effect on k_2 is quite small; the ratio k_2/k_2^* is probably within a factor of 2, even after allowing for the small difference in the temperature. Since reaction 21 represents the transfer of three hydrogen atoms, the small isotope effect, together with the high absolute value of k_2 , suggests that the rate is diffusion controlled in H₂O and perhaps not quite diffusion controlled in HOD-D₂O.

Conclusion

Our results pose a dilemma that we have not as yet resolved. It is clear that aluminum ion interacts strongly with nearby water molecules, and the kinetic unit that is formed is probably larger than $Al(OH_2)_6^{3+}$ and includes water molecules in the second solvent shell or beyond. In agreement with this model, the reaction of $Al(OH_2)_6^{3+}$ with $Al(OH_2)_5OH^{2+}$ shows the characteristics that we expect for proton transfer involving hydrated, hydrogen-bonded ions: the number of water molecules that participate is at least two, k_2 is large, and k_H for the $AlOH$ hydrate is relatively small. Facile proton transfer through the second solvent shell is evidently possible. Yet in the related process of acid dissociation, proton transfer through the second solvent shell does not occur and the H_3O^+ ion dissociates directly from site a. This result is unexpected, indeed unreasonable, yet we have taken pains to prove it and we regard it as experimentally secure.

Experimental Part

Reagents and Solutions. Aluminum chloride hexahydrate, sodium chloride, hydrochloric acid, water, and deuterium oxide were commercial reagent grade chemicals of high purity. The $AlCl_3 \cdot 6H_2O$ reagent was about 1% hydrolyzed, on the basis of pH measurements of its aqueous solutions and its chloride titer, which was 99.67% of theory for $AlCl_3 \cdot 6H_2O$.

Reaction mixtures were prepared by standard quantitative procedures. In each series of experiments, the $AlCl_3$ concentration was approximately constant while the HCl concentration varied widely. For the more acid solutions it was assumed that $[H^+]$ is equal to the molar concentration of added HCl . These solutions served as pH standards for the given series and were used to standardize a Beckman research pH meter. The smaller H^+ concentrations in the series were then measured on the pH meter. Solutions

in HOD-D₂O contained an approximately constant 6 atom % of H which was introduced as $AlCl_3 \cdot 6H_2O$, standard hydrochloric acid, or H_2O .

Nmr Measurements. Measurements of T_2 by spin-echo and of T_1 and control and measurement of the temperature in the nmr probe were the same as described in previous papers from this laboratory.¹⁵ For H_2O acidified with a trace of HCl , we found that $T_1 = 3.0$ sec and $T_2 = 2.8_5$ sec at 29.9°. Since this small difference is barely outside the experimental error, we have interpreted the difference, $(1/T_2) - (1/T_1)$, for the $AlCl_3$ -containing solutions as exchange broadening, according to eq 5.

The precision, and probable accuracy of T_2 and T_1 in H_2O was about $\pm 2\%$, and that of $[(1/T_2) - (1/T_1)]/p$ was $\pm 3\%$. Measurements of T_2 in HOD-D₂O were more difficult because of the smaller signal; we estimate the accuracy to be about $\pm 4\%$. $1/T_1$ in HOD-D₂O is quite small and could be measured directly only at the lowest temperature, near 0°. At that temperature $T_1^{H_2O}/T_1^{HOD-D_2O}$ was found to be 0.265. At the higher temperatures, $1/T_1^{HOD-D_2O}$ was estimated as $0.265/T_1^{H_2O}$ with sufficient accuracy for evaluating $(1/T_2) - (1/T_1)$ in HOD-D₂O.

The chemical shift difference δ between the OH protons in $Al(OH_2)_6^{3+}$ and those in bulk H_2O was determined by measuring $[(1/T_2) - (1/T_1)]/p$ as a function of temperature, as shown in Figure 1. The maximum, which equals $\delta/2$ according to eq 5, gave $\delta = 2000$ sec⁻¹ in H_2O . However, if we assume that the rate must follow an Arrhenius equation, we get best fit of $-\log \tau$ vs. $1/T(^{\circ}K)$ if $\delta = 1960$ sec⁻¹ (5.53 ppm at the resonance frequency of 56.4 MHz). The latter value was used in interpreting the nmr results. To obtain δ in HOD-D₂O, we recorded the nmr spectrum of 2 M $AlCl_3$ -0.02 M HCl at -38.3° in slow passage for both H_2O and HOD-D₂O. At that temperature and pH, proton exchange is sufficiently slow so that protons in the coordination shell and in the bulk solvent give separate nmr signals.⁴ Because of the much higher $AlCl_3$ concentration and lower temperature we did not expect that absolute values of δ would be identical with those in dilute solution, but we hoped that the solvent isotope effects on δ would be approximately independent of conditions. We found that at -38.3° in 2 M $AlCl_3$ -0.02 M HCl , $\delta^{H_2O} = 1590 \pm 37$ sec⁻¹ and $\delta^{HOD-D_2O} = 1524 \pm 7$ sec⁻¹. Assuming an equal difference under the conditions of the rate measurements, and using $\delta^{H_2O} = 1960$ sec⁻¹, we obtained $\delta^{HOD-D_2O} = 1900$ sec⁻¹, rounded to three significant figures. This value was used in all rate calculations.

To investigate fractionation of H isotopes between aluminum hexahydrate and water, we introduce a fractionation factor Φ , defined by $\Phi =$ (proton fraction/site fraction) of aluminum hexahydrate. It then follows that in eq 5, $p\Phi$ must be written instead of p , and $[(1/T_2) - (1/T_1)]_{max} = p\Phi\delta/2$. Thus, according to the experimental results for HOD-D₂O shown in Figure 1, $\Phi\delta = 1990 \pm 120$ sec⁻¹. Since $\delta = 1900$ sec⁻¹, $\Phi = 1.05 \pm 0.06$. An alternate approach is to measure the proton fraction directly by measuring the area under the coordination shell and bulk water nmr signals. For 2 M $AlCl_3$ -0.02 M HCl in HOD-D₂O at -38.3° , Φ was thus found to be 0.93 ± 0.09 . Both values could be unity, within their experimental error. If we assume that $\Phi = 1$ and $\delta = 1900$ sec⁻¹ in HOD-D₂O, values of $-\log \tau$ calculated from the data points in Figure 1 vary with temperature according to an Arrhenius equation, and the fit is very good (see eq 17).

T_1 of $Al(OH_2)_6^{3+}$ Protons. In connection with the nmr measurements of proton exchange rates, we observed that $1/T_1$ of acidified aqueous $AlCl_3$ varies with the $AlCl_3$ concentration by much more than one would predict on the basis of the relative viscosity, η/η_0 . Our results are summarized in Table V. Under the present conditions, proton exchange is sufficiently fast so that

$1/T_1$ is the weighted average of $1/T_1$ in the coordination shell and in bulk water.³⁰ If we assume that $1/T_{1,\text{bulk}}$ in bulk water varies as η/η_0 , then $1/T_{1,\text{cs}}$ in the coordination shell can be deduced from

$$\eta_0/\eta T_1 = (1 - p)/T_{1,\text{bulk}} + p/T_{1,\text{cs}} \quad (34)$$

The fit of eq 34 is satisfactory, and $1/T_{1,\text{cs}} \approx 6.0 \pm 0.3 \text{ sec}^{-1}$. $1/T_{1,\text{cs}}$ can provide a rough measure of the radius of the rotating

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hydrated aluminum ion, on the following basis. In diffusion, the radius of hydrated aluminum ion is larger than that of $\text{Al}(\text{OH}_2)_6^{3+}$. If we assume, therefore, that water molecules adjacent to $\text{Al}(\text{OH}_2)_6^{3+}$ are "irrotationally" bound,²³ then proton spin relaxation in $\text{Al}(\text{OH}_2)_6^{3+}$ is due to fluctuations of the magnetic field resulting from rotation of the hydrated ion. On applying the model of a sphere in a viscous fluid, proposed by Bloembergen, Purcell, and Pound,³¹ we calculate the radius of the rotating sphere to be 5.05 Å.

(31) Reference 8, p 202.

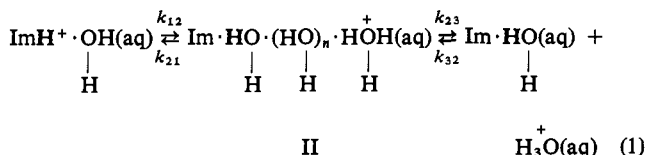
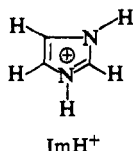
Kinetics of Proton Exchange in the Ionization and Acid Dissociation of Imidazole in Aqueous Acid¹

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Abstract: Rates of proton exchange of imidazolium ion (ImH^+) have been measured in aqueous acid by the nmr method over a wide range of conditions. The rate law is unusually complex. A comparison of rates of proton exchange with rates of relaxation subsequent to temperature jump shows that acid dissociation of the imidazolium ion occurs in two distinct steps, ionization and dissociation. The immediate product of ionization (II, see text) makes a contribution to the rate of proton exchange by the breaking of the $\text{Im}\cdot\text{HOH}$ hydrogen bond. Dissociation of this ionized intermediate appears to be distinctly slower than 10^{11} sec^{-1} . Criteria for the general detection of ionized intermediates are discussed.

The acid dissociation of a Brønsted acid is usefully discussed as involving two distinct steps, ionization and dissociation, as illustrated for imidazolium ion (ImH^+) in water in eq 1. The current view is that for a weak acid the rate constant for the reversal of the ionization step (k_{21} in eq 1) is extremely high, while the rate of dissociation is limited by the rate of diffusion.²⁻⁴



We wish to report a kinetic study of proton exchange between imidazolium ion and water in aqueous solution over a wide range of pH, in which the ionized state, II, is

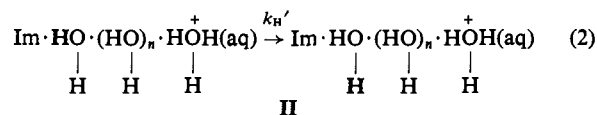
(1) Work supported in part by the National Science Foundation and by the Petroleum Research Fund of the American Chemical Society. Grateful acknowledgment is made to that foundation and to the donors of that fund.

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(3) M. M. Kreevoy and C. A. Mead, *Discussions Faraday Soc.*, **39**, 166 (1965).

(4) E. Grunwald, *Progr. Phys. Org. Chem.*, **3**, 317 (1965).

detected as a reactive intermediate. Detection is possible because the $\text{N}\cdot\text{HOH}$ hydrogen bond is broken at a rate, $k_{H'}$, that is comparable to k_{23} . A possible mechanism is shown in eq 2.



Our data also evaluate the rate constant for the over-all process of acid dissociation. The result is in good agreement with a value determined by the temperature-jump method.⁵ Moreover, our data evaluate the rate constant for breaking the $\text{N}\cdot\text{HOH}$ hydrogen bond in the product, $\text{Im}\cdot\text{HOH}(\text{aq})$.

Experimental Section

Materials. Imidazole (Eastman) was recrystallized from benzene, equiv wt 68.28 (calcd 68.08). Solutions of imidazole in aqueous HCl were prepared by standard analytical techniques.

Nmr Measurements. The exchange broadening of the dominant water resonance was determined in air-saturated solutions by spin-echo measurements⁶ of the transverse (T_2) and longitudinal (T_1) relaxation times at 56.4 MHz. Exchange broadening was equal to $(1/T_2) - (1/T_1)$.

Three parameters are needed to convert the experimental ex-

(5) (a) M. Eigen, G. G. Hammes, and K. Kustin, *J. Amer. Chem. Soc.*, **82**, 3482 (1960); (b) G. G. Hammes, private communication to the authors, Aug 29, 1967.

(6) E. Grunwald and E. Price, *J. Amer. Chem. Soc.*, **86**, 2965, 2970 (1964).