Hydrogen-Ion-Catalyzed Proton Exchange in *t*-Butyl Alcohol-Water Mixtures[1]

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Contribution from the Lecks Chemical Laboratories, Brandeis University, Waltham, Massachusetts 02154. *Received October 10, 1968*

Abstract: Rate constants for hydrogen-ion-catalyzed proton exchange between water molecules, and between water and *t*-BuOH molecules, have been measured separately by the nmr method in 11.47 mole % *t*-BuOH–88.53 mole % H_2O. The two rate constants are very high and nearly equal. Inasmuch as water is more basic than *t*-BuOH, the results show that H_3O^+ is solvated not only by water molecules but also by *t*-BuOH molecules. The alcohol–water reaction is thought to be termolecular, $H_2OH^+ + t\text{-BuOH} + OH_2$, with concerted proton addition and abstraction on *t*-BuOH. The rate constant for the H^+-catalyzed water–water exchange in the *t*-BuOH–H_2O solvent is only 30% smaller than the rate constant in pure water, in spite of the nearly fourfold increase in solvent viscosity.

The anomalous conductance of hydrogen ion in hydroxylic solvents has been the object of keen interest for many years. Meiboom[2] has shown, by nuclear magnetic resonance (nmr) measurements, that anomalous conductance results entirely from proton transfer between the lyonium ion and adjacent solvent molecules. It is well known that when alcohol is added to water, the physical properties are quite nonideal.[3] For example, the viscosity, η, and the Walden product of the anomalous equivalent conductance, $(\lambda^0_{H^+} - \lambda^0_{K^+})\eta$, both rise to a maximum.[3,4]

We now report some nmr measurements of acid-catalyzed proton exchange in the system *t*-butyl alcohol–water, a system in which the peculiar alcohol–water effects are pronounced.[3] The new data include measurements of the rates of acid-catalyzed exchange between water molecules and between water and *t*-BuOH molecules, and various measures of molecular mobility, including nuclear magnetic relaxation times. Rates of proton exchange in alcohol–water mixtures have been reported previously,[5-7] but our results are more amenable to kinetic analysis because we have controlled the pH by means of buffers.

We find that in 11.47 mole % *t*-BuOH–88.53 mole % water, acid-catalyzed proton exchange is only slightly slower than in water, in spite of a fourfold increase in viscosity. The specific rate for reaction between water molecules is 70% of that in pure water; that for reaction between water and alcohol molecules is almost as fast. We regard the high specific rate of acid-catalyzed reaction between water and *t*-BuOH as being highly significant because it suggests that the solvent shell around the lyonium ion contains both alcohol and water molecules.

Experimental Section

Materials. *t*-Butyl alcohol (Eastman) was refluxed and then distilled from calcium hydride, bp 81.8–82.0°. The purification of imidazole is described elsewhere.[8] The solutions containing $H_2{}^{17}O$ were prepared from Yeda material containing 3.58 atom % ^{17}O normalized to natural abundance in hydrogen isotopes. The $H_2{}^{17}O$ was distilled to remove any paramagnetic impurities.

pH Control. The pH was adjusted by using buffers of imidazole–imidazolium chloride. The pH was calculated on the basis of the known acid dissociation constant.[8b]

Viscosity. Viscosities of *t*-BuOH–H_2O mixtures containing from 0 to 11.47 mole % *t*-BuOH were measured at 25.00 ± 0.02° with a Canon Fenske viscometer using water as a reference. The results at the various *t*-BuOH mole fractions are mole % *t*-BuOH, η (centipoise): 0.00, 0.890; 0.59, 0.988; 1.44, 1.18; 3.08, 1.61; 3.99, 1.85; 4.96, 2.13; 6.92, 2.61; 9.50, 3.70; 11.47, 3.43.

Nmr Measurements. Spin–echo measurements were made of the transverse (T_2) and longitudinal (T_1) relaxation times of the solvent OH protons as previously described.[8a] Interference from the methyl proton resonance of *t*-BuOH was removed by the method of Alexander.[9] The resonance frequency was 56.4 MHz, and the sample temperature is accurate to ±0.1°.

Results

We shall let R_{AW} denote the rate of proton transfer from *t*-BuOH to H_2O, R_{WA} that from H_2O to *t*-BuOH, and R_{WW} the rate of proton transfer from H_2O to H_2O; and we shall express these quantities in units of gram-atoms/(liter second). These rates are measurable by the nmr method at hydrogen ion concentrations ranging from 10^{-6} to 10^{-8} *M*. To make a kinetic analysis it was essential to control the pH by means of buffers; we used imidazolium chloride and imidazole. This method introduces the complication that the buffer components react also. The kinetics of proton exchange between buffer and solvent was studied as part of this investigation, and the results are reported in an accompanying paper.[8b]

R_{AW}. To evaluate R_{AW}, we measured the exchange broadening of the OH-proton resonance. The buffer concentration was small in these experiments, so that both kinetic and magnetic effects of the buffer could be neglected. Since the *t*-BuOH contributes only a small fraction (0.065) to the total OH-proton resonance, R_{AW} was calculated from the data according to the theory of "broadening of the dominant nmr line."[2,10] The OH-proton chemical shift, δ, between *t*-BuOH and H_2O is

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[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.

[2] S. Meiboom, *J. Chem. Phys.*, 34, 375 (1961).

[3] F. Franks and D. J. G. Ives, *Quart. Rev.* (London), 20, 1 (1966).

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[6] W. G. Patterson and H. Spedding, *Can. J. Chem.*, 41, 2477 (1963).

[7] W. G. Patterson, *ibid.*, 41, 714, 2472 (1963).

[8] (a) E. K. Ralph and E. Grunwald, *J. Amer. Chem. Soc.*, 91, 2422 (1969); (b) *ibid.*, 91, 2429 (1969).

[9] S. Alexander, *Rev. Sci. Instr.*, 32, 1066 (1961).

[10] E. Grunwald and M. S. Puar, *J. Phys. Chem.*, 71, 1842 (1967), especially eq 8–11.

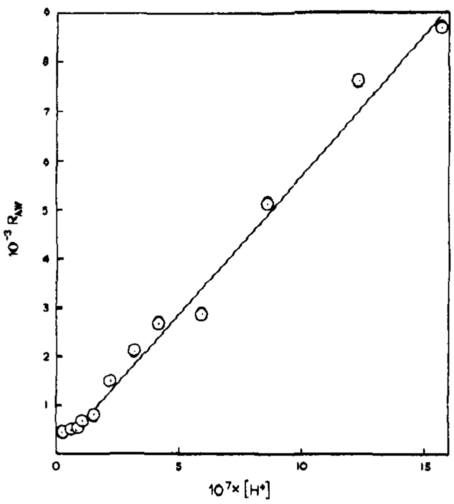

Figure 1. Rate of alcohol-water exchange in 11.47 mole % *t*-BuOH at 25°. The straight line represents eq 1.

obtained also in this treatment, from the maximum broadening of the "dominant line."[10] The value obtained in this way for 11.47 mole % *t*-BuOH–HOH was 0.517 ppm at 25°. This value may be compared with the value, 0.480 ppm, measured at 25° in 67.24 mole % *t*-BuOH–HOH, where both OH resonances are observable in slow passage.

Results for R_{AW} as a function of hydrogen ion concentration in 11.47 mole % *t*-BuOH–HOH at 25° are shown in Figure 1. When $[H^+] > 10^{-7}$ *M*, the rate law is given by

$$R_{AW} = (5.7 \pm 0.2) \times 10^9 [H^+] \qquad (1)$$

Below 10^{-7} *M*, R_{AW} appears to become progressively greater than predicted by eq 1. The deviations are barely significant and probably represent catalysis by lyate ion.

R_{WW}. Meiboom has developed nmr methods for measuring R_{WW} in water enriched in ^{17}O.[2,11] These methods may be applied to our *t*-BuOH–HOH systems in good approximation. In the experiments to be described, we used 11.47 mole % *t*-BuOH–HOH at pH 6.9 in which the water component contained 1.36 atom % of ^{17}O. Exchange of *oxygen* isotopes between H_2O and *t*-BuOH under these conditions is negligibly slow.[12]

In Meiboom's theory protons of $H_2{}^{17}O$ exchange with protons of $H_2{}^{16}O$ and $H_2{}^{18}O$; thus the fraction of ^{17}OH protons in the water solvent is easily defined. In our mixed solvent, however, the presence of exchangeable OH protons of *t*-BuOH poses the mild problem of how best to define the ^{17}OH proton fraction, whether with respect to the water molecules alone or with respect to *all* OH protons, including those of *t*-BuOH. Since in the absence of ^{17}O enrichment the OH-proton resonance is collapsed into a single, exchange-averaged line (R_{AW} is high), we have defined the fraction of ^{17}OH protons with respect to all OH protons.

It is convenient to define an exchange broadening, Δ_{O-17}, which is equal to the increase in line width, $1/T_2$, upon enrichment with $H_2{}^{17}O$. In the present system there is some broadening due to R_{AW}; we have assumed that this broadening and Δ_{O-17} are simply additive. Exact additivity of exchange broadening due to multiple exchange processes is expected in the case of (a) fast exchange ($\delta_i\tau_i \ll 1$ for all exchange processes), and (b) one dominant line (the proton population at one resonance frequency is much greater than that at all other frequencies involved in exchange).[13] The present system approximates to these limits. The rate of exchange is then related to Δ_{O-17} according to[2]

$$\begin{aligned}\Delta_{O-17} &= (T_2{}^{-1})_{O-17} - (T_2{}^{-1})_{\text{normal}} \\ &= P/6 \sum_{i=1}^{6} \delta_i{}^2\tau/(1 + \delta_i{}^2\tau^2) \qquad (2)\end{aligned}$$

where $P = 2[H_2O^{17}]/(\text{total OH})$, τ is the mean time a proton resides on a water molecule in one cycle of exchange, and the summation extends over the six components of the H_2O^{17} spin-spin multiplet. Following Meiboom,[2] we introduce a parameter, J_{eff}, which is related to the ^{17}O–H spin-spin interaction J, the T^{I} relaxation time of the ^{17}O nucleus, and τ, as shown in (3).

$$J_{\text{eff}} = JT^{\text{I}}/(T^{\text{I}} + \tau) \qquad (3)$$

The six values of δ_i in (2) are then $\pm J_{\text{eff}}/2$, $\pm 3J_{\text{eff}}/2$, and $\pm 5J_{\text{eff}}/2$. In applying the method to our system, we shall assume that $J = 613\ \text{sec}^{-1}$, same as in water.[11] T^{I} was obtained by adjustment to the data as follows.

Figure 2 shows a plot of $(T_2{}^{-1})_{O-17}$, $(T_2{}^{-1})_{\text{normal}}$, and Δ_{O-17} for a series of imidazole buffers of constant pH of 6.901 and varying buffer concentration in 11.47 mole % *t*-BuOH–H_2O at 25°. In interpreting this plot, we shall assume that $1/\tau$ increases monotonically with buffer concentration.[8b] Note that Δ_{O-17} goes through a maximum. We make use of this maximum to evaluate T^{I}. According to (2) and (3), for a given value of J and T^{I}, Δ_{O-17} increases with $1/\tau$, goes through a maximum, and then decreases. The magnitude of the maximum was calculated using $J = 613\ \text{sec}^{-1}$ and a series of assumed values for T^{I}. Agreement with experiment results when $T^{\text{I}} = 2.3 \times 10^{-3}$ sec.

Having obtained T^{I} by fitting the maximum, the rest of the Δ_{O-17} data was used to define the rate law for proton exchange. The result is (4a), which gives excellent fit, as shown by the solid curve in Figure 2. [Im] and $[ImH^+]$

$$\begin{aligned}1/\tau &= (300 \pm 60) + (3.4 \pm 0.3) \times 10^6[Im][ImH^+] \qquad (4a) \\ &= (2.4 \pm 0.5) \times 10^9[H^+] + (3.4 \pm 0.3) \times 10^6[Im][ImH^+] \qquad (4b)\end{aligned}$$

denote concentrations of the imidazole buffer components.

In order to show that proton exchange is catalyzed by hydrogen ion (lyate-catalyzed proton exchange is negligible at pH 6.901), (4a) is rewritten in the form (4b). The rate constant for acid-catalyzed exchange is then obtained as follows. According to our definitions of P and τ, the exchange is between a labeled water molecule and any OH site; hence $1/\tau = (R_{WW} + R_{WA})/2[H_2O]$. Because of microscopic reversibility, $R_{WA} = R_{AW}$. On substituting numerical values for R_{AW} and $[H_2O]$ (eq 1 and 34.2 *M*, respectively), we obtain

$$R_{WW} = (15.8 \pm 3) \times 10^{10}[H^+] \qquad (5)$$

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[11] Z. Luz and S. Meiboom, *J. Chem. Phys.*, **39**, 366 (1963).

[12] I. Dostrovsky and F. S. Klein, *J. Chem. Soc.*, 791 (1955).

[13] Cases a and b are extensions of the cases discussed by Meiboom in ref 2. We thank Dr. Meiboom for a helpful discussion.

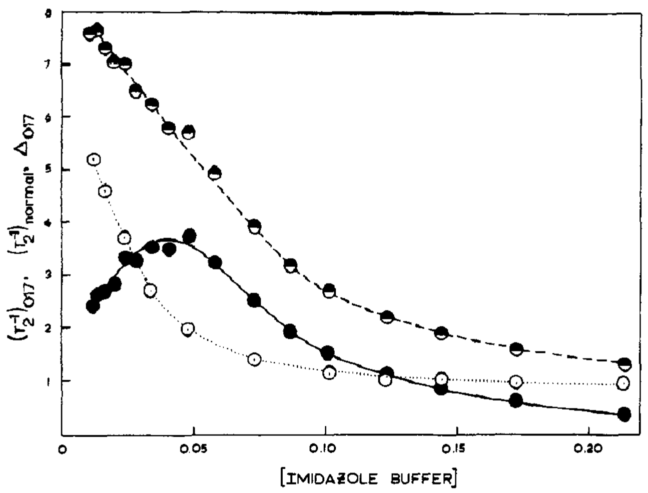
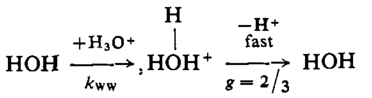


Figure 2. $(1/T_2)_{\mathrm{O-17}}$, $(1/T_2)_{\mathrm{normal}}$, and $\Delta_{\mathrm{O-17}}$ *vs.* imidazole buffer concentration in 11.47 mole % *t*-BuOH at 25°: ○, $(1/T_2)_{\mathrm{normal}}$; ◓, $(1/T_2)_{\mathrm{O-17}}$; ●, $\Delta_{\mathrm{O-17}}$. The solid curve represents the calculated $\Delta_{\mathrm{O-17}}$ according to the rate law (eq 4a).

Discussion

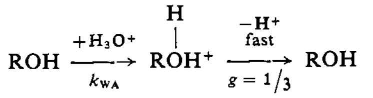
Although there is considerable uncertainty concerning the relative basicity of *t*-BuOH and water in aqueous solutions, there is little doubt that the basicity of water is at least 10 times, and perhaps more than 1000 times, greater.[14] We shall, therefore, assume that the lyonium ion is largely H_3O^+.

We now wish to analyze the experimental rate constants on the basis of a bimolecular mechanism (eq 6 and 7) and show that such a mechanism leads to an implausible result.



$$\mathrm{HOH}\xrightarrow[k_{\mathrm{WW}}]{+\mathrm{H_3O^+}}\overset{\mathrm{H}}{\overset{|}{\mathrm{HOH^+}}}\xrightarrow[g={}^2/_3]{\substack{-\mathrm{H^+}\\ \text{fast}}}\mathrm{HOH} \qquad (6a)$$

$$R_{\mathrm{WW}} = (2/3)k_{\mathrm{WW}}[\mathrm{H^+}][\mathrm{H_2O}] \qquad (6b)$$



$$\mathrm{ROH}\xrightarrow[k_{\mathrm{WA}}]{+\mathrm{H_3O^+}}\overset{\mathrm{H}}{\overset{|}{\mathrm{ROH^+}}}\xrightarrow[g={}^1/_3]{\substack{-\mathrm{H^+}\\ \text{fast}}}\mathrm{ROH} \qquad (7a)$$

$$R_{\mathrm{AW}} = (1/2)k_{\mathrm{WA}}[\mathrm{H^+}][\mathrm{ROH}] \qquad (7b)$$

In eq 6a, which depicts bimolecular water–water exchange, a proton is added to a water molecular in a first, rate-determining step. The resultant H_3O^+ then reacts rapidly; the probability, g, that reaction leads to proton exchange is ${}^2/_3$. Equation 7a analogously depicts bimolecular alcohol–water exchange; g is now ½. In both processes, the hydrogen ion reacting in the rate-determining step is almost entirely H_3O^+.

The corresponding rate laws are 6b and 7b. The rate constants, k_{WW} and k_{WA}, can be evaluated by comparing these equations with the experimental rate laws (1) and (5); in 11.47 mole % *t*-BuOH, $H_2O = 34.2\ M$ and *t*-BuOH = 4.43 *M*. Thus we obtain

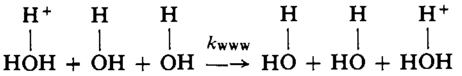
$$k_{\mathrm{WW}} = 6.9 \times 10^9\ M^{-1}\ \mathrm{sec}^{-1}$$

$$k_{\mathrm{WA}} = 2.5_6 \times 10^9\ M^{-1}\ \mathrm{sec}^{-1}$$

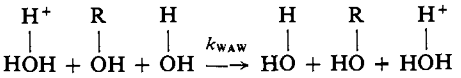
$$k_{\mathrm{WW}}/k_{\mathrm{WA}} = 2.7$$

Recalling that water is at least ten times more basic than *t*-BuOH, the ratio $k_{\mathrm{WW}}/k_{\mathrm{WA}}$ strikes us as implausibly small.

While in the bimolecular mechanism the product of reaction of H_3O^+ with *t*-BuOH must be the unstable *t*-$\mathrm{BuOH_2}^+$, a termolecular mechanism (eq 8 and 9) permits proton exchange while avoiding formation of this ion. The ratio $k_{\mathrm{WWW}}/k_{\mathrm{WAW}}$ can be obtained from the



$$\begin{array}{c}\mathrm{H^+}\\|\\\mathrm{HOH}\end{array}+\begin{array}{c}\mathrm{H}\\|\\\mathrm{OH}\end{array}+\begin{array}{c}\mathrm{H}\\|\\\mathrm{OH}\end{array}\xrightarrow{k_{\mathrm{WWW}}}\begin{array}{c}\mathrm{H}\\|\\\mathrm{HO}\end{array}+\begin{array}{c}\mathrm{H}\\|\\\mathrm{HO}\end{array}+\begin{array}{c}\mathrm{H^+}\\|\\\mathrm{HOH}\end{array} \qquad (8)$$



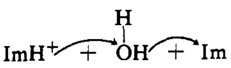
$$\begin{array}{c}\mathrm{H^+}\\|\\\mathrm{HOH}\end{array}+\begin{array}{c}\mathrm{R}\\|\\\mathrm{OH}\end{array}+\begin{array}{c}\mathrm{H}\\|\\\mathrm{OH}\end{array}\xrightarrow{k_{\mathrm{WAW}}}\begin{array}{c}\mathrm{H}\\|\\\mathrm{HO}\end{array}+\begin{array}{c}\mathrm{R}\\|\\\mathrm{HO}\end{array}+\begin{array}{c}\mathrm{H^+}\\|\\\mathrm{HOH}\end{array} \qquad (9)$$

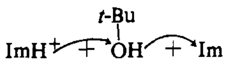
experimental data in the same way as before, except that the statistical factors are different from those used in the bimolecular mechanism. In (8), if the $\mathrm{H_2O{\cdot}HOH_2}^+$ hydrogen bond breaks after each step, $g_8 = 2$; if (8) is the elementary step in a mechanism of structural diffusion, $g_8 = {}^4/_3$.[15] In (9), both mechanisms lead to $g = 1$, either exactly or in close approximation. Thus we obtain

$$k_{\mathrm{WWW}}/k_{\mathrm{WAW}} = 1.8\ (g_8 = 2)$$

$$\text{or} = 2.7\ (g_8 = {}^4/_3)$$

A specific reactivity ratio near 2 is a plausible result for a termolecular mechanism. First of all, a previous study[16] of the analogous reaction of phenols in methanol has shown that termolecular rate constants tend to increase with the basicity of the central, amphiprotic molecule, other things being equal. However, the increase is considerably less than proportional to K_{B}. We can make a crude estimate of the magnitude of this factor on the basis of the ratio of specific rates for termolecular processes involving imidazole buffer.





Measurements of this ratio are reported in the accompanying paper;[8b] the value found for 11.47 mole % *t*-BuOH at 25° is 1.75, of precisely the same magnitude as $k_{\mathrm{WWW}}/k_{\mathrm{WAW}}$.

There is of course no necessity for R_{WW} and R_{AW} to involve the same reaction mechanism. However, if we insist that the mechanisms be the same, then a termolecular model seems to fit better than a bimolecular model. If we do not so insist, then the termolecular model still seems to be preferable for R_{AW} on the basis of a number of arguments: the analogous reaction of hydrogen ion with phenol is termolecular;[10] the absolute value of R_{AW} is unreasonably high for a reaction that proceeds by the bimolecular mechanism 7a; and R_{AW} for acid-catalyzed proton exchange appears to become relatively very slow in alcohol containing only a small mole fraction of water.[5]

Regardless of mechanism, our data shed light on the

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[14] For recent reviews, see R. E. Weston, S. Ehrenson, and K. Heinzinger, *J. Amer. Chem. Soc.*, **89**, 481 (1967); E. M. Arnett, *Progr. Phys. Org. Chem.*, **1**, 223 (1963).

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[16] M. S. Puar and E. Grunwald, *Tetrahedron*, **24**, 2603 (1968).

Table I. Measures of Molecular Mobility and Acid-Catalyzed Proton Exchange in the System t-BuOH–H_2O at 25°

Property	Mole % t-BuOH 0.00	Mole % t-BuOH 11.47	Ratio
η, Cp	0.89	3.43	3.86
$1/T_1$ for OH protons, sec^{-1}	0.39^a	0.90^a	2.3
E_{act}, kcal, for T_1	3.6	6.6	...
$1/T^I$ for ^{17}O in $H_2{}^{17}O$, sec^{-1}	$160^{a,b}$	440^a	2.75
$R_{WW}/[H^+][H_2O]$, sec^{-1} M^{-1}	7.1×10^{9c}	4.6×10^9	1.5_5

[a] All T_1 measurements were made in air-saturated solvent. [b] Reference 11, and B. B. Garrett, A. B. Denison, and S. W. Rabideau, *J. Phys. Chem.*, **71**, 2606 (1967). [c] The value listed in this table is $2k_1/3$, as reported by Meiboom.[2]

solvation of H_3O^+ in the t-BuOH–HOH system. There is no doubt that the specific rate for reaction between H_3O^+ and alcohol is only slightly smaller than that for the reaction between H_3O^+ and water. This is possible only if the distribution of molecules around the H_3O^+ ion is nearly statistical; that is, a model of strong preferential solvation of H_3O^+ by water molecules seems to be ruled out.

Regarding R_{WW}, our data permit comparison of the specific rate in pure water with that in 11.47 mole % t-BuOH–HOH. As shown in Table I, the specific rate decreases by a factor of 1.55, while the viscosity increases by a factor of 3.86. Thus the "Walden product," (specific rate)·η, increases by 2.5, in good qualitative agreement with the Walden product for the anomalous conductance. On the other hand, the solvent effect on the specific rate is in better agreement with that on the OH-proton T_1, or on the ^{17}O T^I, which in a rough way measure the rate of rotation of the water molecules.

Proton Exchange and Solvation of Imidazole in t-Butyl Alcohol–Water Mixtures[1]

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Abstract: Effects of specific solvation on proton transfer of imidazolium ion (ImH^+) have been studied in t-BuOH–HOH mixtures by nmr measurements of proton-exchange rates and by potentiometric measurements of pK_A. Processes that make significant kinetic contributions to proton exchange are acid dissociation, the mechanism of which is found to be analogous to that in water, and the termolecular reactions, $ImH^+ + (OH)H + Im \rightarrow Im + HOH + HIm^+$ (k_{2W}), and $ImH^+ + (OBu\text{-}t)H + Im \rightarrow Im + HOBu\text{-}t + HIm^+$ (k_{2A}). In 11.47 mole % t-BuOH at 25°, $k_{2W} = 2.0 \times 10^8$ sec^{-1} M^{-1} and $k_{2A} = 1.57 \times 10^7$ sec^{-1} M^{-1}. The magnitude of k_{2W}/k_{2A} is very similar to that of the $[H_2O]/[t\text{-BuOH}]$ mole ratio, suggesting that the relative abundance of the respective termolecular encounter complexes is nearly statistical. k_{2W} is strikingly greater in the t-BuOH–HOH mixtures than in water.

Kinetic analysis of proton exchange accompanying fast proton-transfer reactions can provide new information about solvation, especially when the rate-determining step is the solvation or desolvation of one of the reacting species.[2] The present paper is the first of a series in which we use this technique to study preferential solvation in t-butyl alcohol–water mixtures. This system is suitable for such a study because precise nmr measurements of the rates of exchange are possible. Rates of exchange can be measured separately for alcohol OH protons and water OH protons. The system is chemically interesting, and thermodynamic studies suggest that specific solvation effects may be pronounced.[3] Our own interest would center on the kinetic effects of specific solvation, especially on the relative rates of breaking of solute–water and solute–HOBu-t hydrogen-bonded complexes. We would expect those rates to be quite different if the solute–solvent interaction is dominated by London dispersion forces.[4]

In this paper we report a study of proton exchange of imidazolium ion (ImH^+) in t-BuOH–water mixtures containing 9.98 and 11.47 mole % t-BuOH. Rates were measured by the nmr method at temperatures ranging

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(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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