sults reported with the tetrafluoroborate anion, hexafluorosilicate salts of large cations such as Bu_4N^+ might absorb silicon tetrafluoride to give complex fluorosilicate anions.

Further details of the dehydrofluorination reactions will be reported in subsequent articles.

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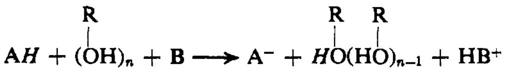
Higher-than-Termolecular Proton Transfer in Aqueous Solutions of Imidazole[1]

Sir:

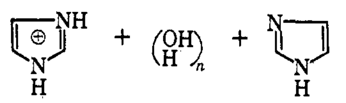
Three mechanisms for proton transfer are commonly recognized: direct bimolecular reaction of an acid with a base; termolecular reaction in which an acid donates a proton to a substrate while a base abstracts a (different) proton from the substrate; and, in hydroxylic solvents, acid–base reaction by a Grotthus mechanism such as (1), in which n solvent molecules participate.



$$\mathrm{A}H + (\overset{\mathrm{R}}{\overset{|}{\mathrm{O}}}\mathrm{H})_n + \mathrm{B} \longrightarrow \mathrm{A}^- + H\overset{\mathrm{R}}{\overset{|}{\mathrm{O}}}(\mathrm{H}\overset{\mathrm{R}}{\overset{|}{\mathrm{O}}})_{n-1} + \mathrm{HB}^+ \qquad (1)$$

By means of nuclear magnetic resonance, it is possible to measure the rates of proton exchange resulting from (1) independently for the acid and the solvent, and thus to obtain directly the number, n, of solvent molecules.[2,3] This experiment has been tried on a number of systems. Examples are phenol (HA) and methoxide ion (B) in methanol (ROH); Me_3NH^+ and Me_3N in water; benzoic acid and benzoate ion in methanol; and phenol and phenoxide ion in water and methanol.[2-4] Up to now, all such *direct* measurements have led to the result that $n = 1$; that is, the reaction is termolecular.

At the same time, there is strong *indirect* evidence from reaction diameters and proton-exchange kinetics that certain very fast reactions, such as that of H_3O^+ with OH^- or Me_3N, or that of $H_2PO_4^-$ with HPO_4^{2-}, in water involve two or more water molecules.[5-7] We now wish to report a *direct measurement* in which $n > 1$. The reaction is that of imidazolium ion ([ImH$^+$], HA in eq 1) with imidazole ([Im], B in eq 1) in water.



(2)

Rates (R_{NH}) of exchange of NH protons of imidazolium ion with OH protons of water were measured by nuclear magnetic spin–echo techniques, as described previously.[8] Rates (R_{OH}) of proton exchange of water molecules were measured in O^{17}-enriched water, as described by Luz and Meiboom.[3] The resulting rate laws are stated in eq 3–5. Results and standard errors

$$R_{NH} = k_2[\mathrm{ImH^+}][\mathrm{Im}] + 5.9 \times 10^3[\mathrm{ImH^+}] \quad (\mathrm{pH}\ 5.44\text{–}3.74,\ 25.0°,\ [\mathrm{ImH^+}] = 0.07\ M) \qquad (3)$$

$$R_{OH} = k_2'[\mathrm{ImH^+}][\mathrm{Im}] + 3.3 \times 10^{11}[\mathrm{OH^-}] + 3.3 \times 10^{11}[\mathrm{H^+}] \quad (\mathrm{pH}\ 6.587,\ 25.0°,\ [\mathrm{ImH^+}] < 0.26\ M) \qquad (4)$$

$$k_2' = nk_2 \qquad (5)$$

at 25° are $k_2' = (1.52 \pm 0.15) \times 10^8\ \mathrm{sec}^{-1}\ M^{-1}$; $k_2 = (1.07 \pm 0.11) \times 10^8\ \mathrm{sec}^{-1}\ M^{-1}$; $n = 1.42 \pm 0.19$.[9]

The number, $n = 1.42$, must be interpreted as an *average*. Since direct bimolecular proton transfer contributes neither to R_{NH} nor to R_{OH}, the smallest value that n can take is unity. Hence, in (2), somewhat more than half of the individual events are termolecular, while the others are quadrimolecular or higher. If we arbitrarily rule out $n > 2$, then the fraction of $n = 1$ is 0.58 and that of $n = 2$ is 0.42.

We believe that the average value for n in reactions of the general type 1 is closely related to the strength of the hydrogen-bonded solvation complexes. Consider the conversion of the quadrimolecular to the termolecular encounter complex (eq 6). Of the two

$$\mathrm{AH}\cdot\overset{\mathrm{R}}{\mathrm{O}}\mathrm{H}\cdot\cdot\overset{\mathrm{R}}{\mathrm{O}}\mathrm{H}\cdot\mathrm{B} \longrightarrow \mathrm{AH}\cdot\overset{\mathrm{R}}{\mathrm{O}}\mathrm{H}\cdot\mathrm{B} + \mathrm{ROH}\ (\text{bulk solvent}) \qquad (6)$$

ROH molecules on the left, the one forming the weaker hydrogen bonds will diffuse out more rapidly, so that the rate of eq 6 will reflect largely the properties of that molecule. If the binding is strong, the rate is probably slower than that for diffusion of ROH in bulk solvent. At the same time, the strong binding will probably enhance the Boltzmann factors of those configurations that permit multiple proton transfers.

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[9] The following facts suggest that these standard errors are estimated conservatively. (a) In 11.47 mole % *t*-butyl alcohol–88.53 mole % water, an analogous set of experiments results in $n = 1.01 \pm 0.15$, showing that our method is capable of detecting a value of unity. (b) In eq 4, the contributions to R_{OH} from [OH$^-$] and [H$^+$] are in very good agreement with previous reports: S. Meiboom, *J. Chem. Phys.*, **34**, 375 (1961); A. Loewenstein and A. Szöke, *J. Am. Chem. Soc.*, **84**, 1151 (1962).

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Dielectric Measurements on Triethylamine–Iodine Complex

Sir:

The previous papers of Toyoda and Person[1] and of Kobinata and Nagakura[2] incited us to undertake measurements on triethylamine–iodine mixtures because the values of 11 and 12 D, obtained for the 1:1 complex, are not in good agreement with the values of 4 to 7 D measured on the other amine–iodine complexes.[1-4] Toyoda and others have used dioxane as the solvent because they noticed an instability of the solutions in heptane at the concentration used for dielectric measurements.

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