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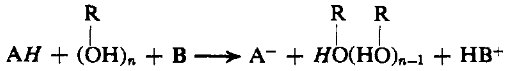
Higher-than-Termolecular Proton Transfer in Aqueous Solutions of Imidazole[1]

Sir:

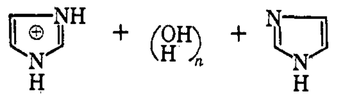
Three mechanisms for proton transfer are commonly recognized: direct bimolecular reaction of an acid with a base; termolecular reaction in which an acid donates a proton to a substrate while a base abstracts a (different) proton from the substrate; and, in hydroxylic solvents, acid–base reaction by a 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

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

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

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

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

(1) Work supported by the National Science Foundation under Grants GP 3921 and 7381 X.

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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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(2) S. Kobinata and S. Nagakura, *ibid.*, **88**, 3905 (1966).

(3) H. Tsubomura and S. Nagakura, *J. Chem. Phys.*, **27**, 819 (1957).

(4) G. Kortüm and H. Walz, *Z. Elektrochem.*, **57**, 73 (1953).

Qualitative Study. Nagakura[5] noticed that the decomposition of solutions in heptane happens quickly, except at very low concentrations. In benzene and dioxane, solutions seem more stable up to concentrations of the order of 10^{-3} *M*, but in both cases, as well as in more polar solvents (ethyl ether), a precipitate appears at sufficiently high concentrations. When there is a large excess of amine, white crystals appear, and, in the case of an excess of iodine, a brown oily precipitate is formed. The analysis of the latter seems difficult, but the white crystals have been identified as triethylamine hydroiodide ($Et_3N \cdot HI$). The compound is very soluble in water and a titration of I^- ions and total iodine gave 53 and 54 wt %. Theoretically, $Et_3N \cdot HI$ contains 55.4% iodide. Besides, a synthetic salt has the same point of decomposition when heated and the dielectric properties of solutions of these two compounds in chloroform are the same (see below).

The solubility of pure triethylamine hydroiodide in heptane and cyclohexane was found to be very low. Benzene and dioxane can dissolve more than 10^{-3} mole/l.; this is sufficient to greatly affect the dielectric measurements.

A study on a WTW Type DM.01 dipolemeter showed that the permittivity of dilute solutions in heptane and cyclohexane is stable during few minutes; afterward, it decreases when precipitation occurs. In the case of dioxane, the permittivity increases during a first stage, which can be short at high concentration, and decreases when the precipitation begins.

Qualitatively, we can conclude that a complex between Et_3N and I_2 is formed instantaneously after mixing and is slowly decomposed to give $Et_3N \cdot HI$ among the products of this decomposition. Solutions in dioxane seem more stable because of the solubility of these compounds. It is not impossible that, in the solution, $Et_3N \cdot HI$ gives complexes as $Et_3N \cdot HI_3$

Dipole Moment of Triethylamine Hydroiodide. Measurements on solutions of $Et_3N \cdot HI$ in dioxane (*ca* 10^{-3} *M*) gave $\mu = 10.6$ D, but the low solubility makes the accuracy of the measurements rather bad. Runs carried out on solutions in chloroform using Onsager's relation, extended to mixtures of polar substances,[6] gave $\mu = 11.6$ D. In these experiments, concentrations up to about 15×10^{-3} *M* could be studied without any trouble from the conductivity, but this result can hardly be compared with the former because of an eventual solvation of $Et_3N \cdot HI$ which may introduce a slight difference on the value of μ. The same value of μ is obtained using the white precipitate mentioned above instead of synthetic hydroiodide.

Dipole Moment of Triethylamine–Iodine Complex. Dielectric measurements are in good agreement with the formation of a 1:1 complex, but the study is only possible with an excess of amine and in very dilute solutions. We worked on solutions ranging from 10 to 20×10^{-3} *M* at room temperature. Under these conditions, solutions in cyclohexane or heptane are stable for a few minutes. The measurement of dipole moment requires knowledge of the equilibrium constant *K* of the reaction

$$Et_3N + I_2 \rightleftharpoons Et_3N \cdot I_2$$

The determination of *K* is possible but not accurate because of the rather restrictive operating conditions. We obtained in cyclohexane at 25° $K = 2.5 \pm 2 \times 10^3$ l./mole and in heptane at 19.5° $K = 3 \pm 2 \times 10^3$ l./mole. The values are comparable with 6.32×10^3 and 4.69×10^3 l./mole obtained in heptane at 20 and 25° by Nagakura.[5] Using the values of *K* given by Nagakura, we obtained for the dipole moment of the complex the values given in Table I.

Table I

	μ, D			
	Run 1	Run 2	Run 3	Run 4
In heptane at 19.5°	5.6	5.5	5.5	5.7
In cyclohexane at 25°	5.0	5.9	5.9	
In dioxane (lit. values)	11.3[3]		12.4[1]	

These results are in good agreement with the dipole moments of complexes formed between iodine and amines given by Kortüm[4] and Kobinata.[2] The large values found by Toyoda[1] and Tsubomura[3] cannot be attributed to an ionic structure of complex but rather to the presence of $Et_3N \cdot HI$ formed by a secondary reaction.

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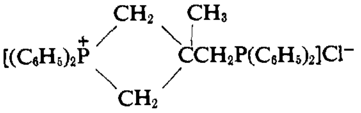
Coordination by a Positively Charged Phosphorus Ligand[1]

Sir:

In marked contrast to the extensive number of investigations with neutral and negatively charged ligands, relatively little work has been reported with positively charged ligands. In fact, the only concerted effort in this area has been undertaken recently by Quagliano, *et al.*,[2–6] in which they investigated the coordination properties of a few diamine ligands where one of the nitrogen atoms was either protonated or alkylated. However, there has been no systematic investigation on the coordination properties of a compound that possesses a quaternary phosphorus or arsenic atom.

This paper reports the preparation and characterization of 3-[(diphenylphosphino)methyl]-3-methyl-1,1-diphenylphosphitanium chloride



and some pseudo-tetrahedral cobalt(II) complexes in

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