

Proton Transfer in Aqueous–Organic Solvents

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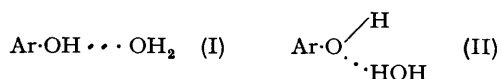
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IN mixed solvents the rates of reactions that generate ions are sensitive to the mole-fraction of water in the solvent, a "medium effect" of this type being ordinarily attributed to changes in solvation and/or dielectric constant. In order to learn more about its origin, we have measured the rate of proton exchange between a phenol and base

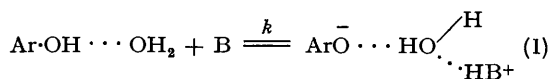
(piperidine) in dioxan–water mixtures containing 0–0.05 mole-fraction of water.

2,6-Di-*t*-butylphenol was chosen for detailed study. In dry dioxan, exchange with piperidine occurs at a low rate which can be neglected in comparison with the rates in presence of water. To analyse the results in aqueous media, the

association constants of the phenol with dioxan (1:1- and 2:1-complexes) were determined from the proton spectrum by routine methods.¹ Since the phenolic oxygen atom is screened by the alkyl groups, this phenol acts only as proton donor in H-bond formation; thus its complex with water is represented by (I), not (II), and its self-association is very weak.¹

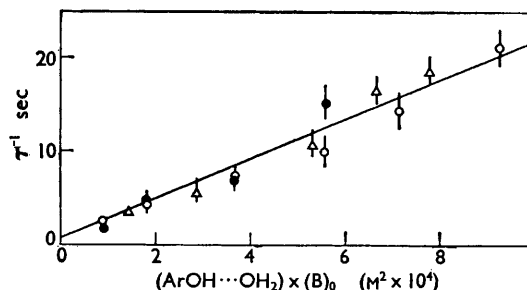


The rates were analysed on the assumption that the dioxan-phenol complexes are kinetically inactive, the phenolic hydrogen being shielded from the base during the lifetime of the complex. In wet solvent, exchange may occur through a concerted process involving simultaneous (or nearly simultaneous) transfer of the proton from the phenol to the H-bonded water molecule, and from the water molecule to the base,



Analogous processes are well established in aqueous² and alcoholic solutions.³ Since we are looking for a molecular explanation of the medium effect, we take k to be independent of the medium and seek to explain the rates in terms of the changing concentration of the complex (I). The rate equation is then $R = k(\text{ArOH}\cdots\text{OH}_2)(\text{B})_0$, the suffix zero signifying total (stoichiometric) concentration. The rates $R = \tau^{-1}(\text{ArOH})_0$ were calculated from the relaxation times τ of the

phenolic-OH and water resonances which remain separate in the useful range of piperidine concentration (10^{-2} — 10^{-3}M). The constant k can be evaluated either from the change of R with $(\text{ArOH}\cdots\text{OH}_2)$ at constant piperidine concentration, or from the change with piperidine concentration at constant water mole-fraction. These two sets gave concordant results and are plotted jointly in the Figure: they give $k(25^\circ) = 2.3 \times 10^4 \text{ mole}^{-1} \text{ l. sec.}^{-1}$. It follows that the mechanism (I) does offer a possible explanation of the rate profile in aqueous dioxan, and it is worth noting that this process corresponds to maximum economy in the use of water molecules to solvate the dipolar transition state.



Circles: $(\text{ArOH})_0 = 1\text{M}$, $(\text{H}_2\text{O})_0 = 0.382\text{M}$, $(\text{B})_0 = 10^{-2}$ — 10^{-3}M [τ from ArOH (\odot) and H_2O (\bullet) resonances]. Triangles: $(\text{ArOH})_0 = 1\text{M}$, $(\text{B})_0 = 4.5 \times 10^{-3}\text{M}$, $(\text{H}_2\text{O})_0 = 0.1$ — 0.6M .

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¹ B. G. Somers and H. S. Gutowsky, *J. Amer. Chem. Soc.*, 1963, **85**, 3065.

² E. Grunwald, *J. Phys. Chem.*, 1963, **67**, 2208, and earlier refs.

³ E. Grunwald and S. Meiboom, *J. Amer. Chem. Soc.*, 1963, **85**, 2047.