

Mechanisms of Aqueous Solvolyses

By MARTYN C. R. SYMONS

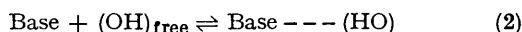
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Summary The concept that water contains an equilibrium concentration of 'free' OH and 'free' lone-pair groups is used to give a qualitative explanation of the large rate

changes observed for certain hydrolyses on the addition of cosolvents. _____

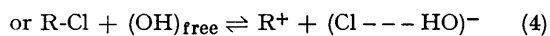
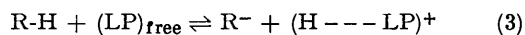
HYDROLYSES initiated by C-H ionization, such as those of certain perchlorates,¹ are greatly accelerated by added alcohols or basic aprotic solvents, and by tetra-alkylammonium halides, but slightly decelerated by other salts. Proton exchange rates for malononitriles behave similarly.² In contrast the rates of hydrolysis of *t*-butyl chloride and a variety of related compounds, thought to proceed *via* an initial ionization to give halide ions, are decelerated in a comparable way by alcohols and basic aprotic solvents.³ Other hydrolyses that are better described as S_N2 are remarkably insensitive to these additives.

These trends are generally discussed in terms of changes in the activities of the solutes or of water, but, so far as I am aware, no explicit description of the mechanisms has previously been put forward. For some years, I and others have stressed the spectroscopic importance of free (OH) groups in liquid water.⁴⁻⁶ It is suggested that (OH)_{free} groups can be detected in the overtone regions of the O-H stretching band for water,⁴⁻⁶ but the corresponding free 'lone-pair' units, (LP)_{free}, have not been detected by direct spectroscopic means. Clearly, the fraction of such groups (probably between 4 and 8% based on the total water concentration)⁷ must be equal in pure water, but when a basic cosolvent is added, the concentration of (OH)_{free} should fall, and that of (LP)_{free} should rise [reactions (1) and (2)]. The loss of (OH)_{free} is indeed observed in the

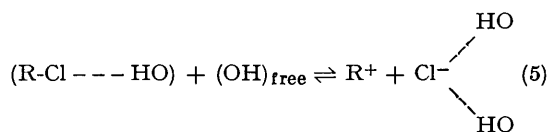


overtone i.r. spectrum, as predicted by reactions (1) and (2). Furthermore, we have concluded⁷ that equilibrium (2) completely favours the hydrogen-bonded form for all soluble bases. [I stress that the (OH)_{free} and (LP)_{free} groups are envisaged as being statistically distributed so that the law of mass-action is followed, rather than remaining together in some form of stretched or broken bond.] Methanol acts as a mono-base, as judged by its effect on the overtone band of HOD. In my view this property, which is also shown by other alcohols, can be understood in terms of the formation of three hydrogen bonds by methanol in dilute aqueous solution. Thus these alcohols behave, in effect, as weak mono-bases.

My suggestion is that these 'free' groups are the reactive ingredients in many reactions of water, fully hydrogen-bonded water molecules being relatively inactive. Hence, induced changes in rate such as those mentioned above simply reflect changes in the concentration of these species. Thus we can write processes such as reactions (3) and (4).



Alternatively, processes such as (5) can be envisaged.



Qualitatively, reactions (3)–(5) explain the observed changes, since reactions (4) or (5) will become slower as the concentration of (OH)_{free} groups falls according to re-

actions (1) and (2), whilst reaction (3) will become faster as the concentration of (LP)_{free} groups increases.

I have recently suggested that many details of Engbert's reaction (6) can be understood using this simple hypothesis.⁸ As an example, addition of 0.1 mole fraction of dioxan



causes the rate constant to increase from 32.5 to 111.0 s⁻¹. I predict that the rate should increase according to (7).

$$k_{\text{diox}} = k_{\text{H}_2\text{O}} \times [\text{LP}]_{\text{diox}} / [\text{LP}]_{\text{H}_2\text{O}} \quad (7)$$

The above equilibrium and the law of mass action gives $k_{\text{diox}} = 104.4 \text{ s}^{-1}$, if dioxan is treated as being dibasic, and an initial concentration of 8% (mole fraction) is taken for (LP)_{free}. If an initial value of 5% is used, a rate constant of 160 s⁻¹ is predicted. For S_N1 reactions, an equation similar to (7) leads to predicted rate changes that are smaller than those obtained experimentally. However, if reaction (5) is used, then k_{solv} is given by equation (8), and the

$$k_{\text{solv}} = k_{\text{H}_2\text{O}} \times [\text{LP}]_{\text{solv}}^2 / [\text{LP}]_{\text{H}_2\text{O}}^2 \quad (8)$$

predicted rates are close to those observed. The fit is most satisfactory if we assume 5% (mole fraction) dissociation for pure water, as indicated in the Figure. Results taken from

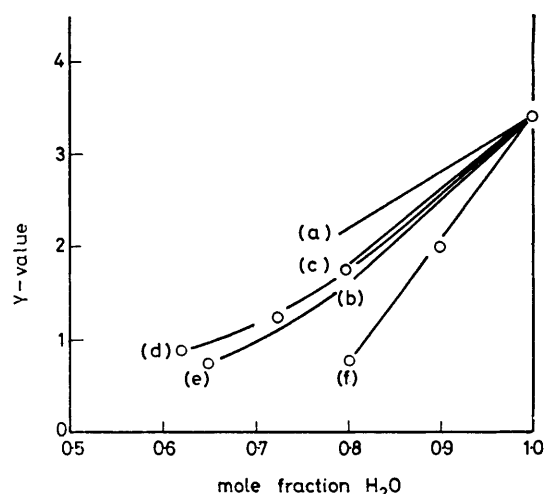


FIGURE. Change in *Y*-value with added basic cosolvents compared with the change predicted using equation (8) together with the assumption of (a) 8% and (b) 5% dissociation into (OH)_{free} and (LP)_{free} in pure water; (c) MeCN, MeOH, and EtOH; (d) Me₂SO; (e) Me₂CO; (f) THF.

the literature are plotted as *Y*-values,³ *Y* being defined as in equation (9) (k_0 = rate constant at 25 °C for 80%

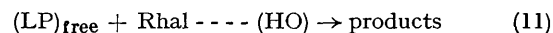
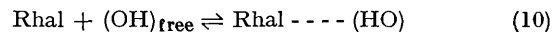
$$Y = \log k - \log k_0 \quad (9)$$

aqueous ethanol).³ The results for methanol,³ ethanol,³ methyl cyanide,⁹ dimethyl sulphoxide,¹⁰ and acetone³ all lie close to the predicted curve. Only results for tetrahydrofuran⁹ (THF) differ significantly. This deviation could be explained if THF acts as a di-base in water, but this seems unlikely. The results strongly suggest that all the other solvents behave as mono-bases that are fully hydrogen-bonded in water.

The reasoning behind equation (5) is as follows. Compounds such as *t*-butyl chloride are sparingly soluble in water. I suggest that this means that they are unable to compete with water molecules for hydrogen bonds, and that water largely rejects non-hydrogen bonded molecules. However, they are able to form very weak hydrogen bonds with the (OH)_{free} groups. The probability of this mono-bonded molecule dissociating (equation 4) is small, but reaction with a second (OH)_{free} group stabilises the incipient chloride ion sufficiently to lead to ionization. It is often implied that ionization is aided by halide solvation of the transition-state. However, it is hard to envisage the formation of hydrogen bonds to chlorine during the time of a vibration. The present postulate overcomes this need, by invoking hydrogen-bonding prior to reaction.

The relative insensitivity of S_N2 type reactions to added

cosolvents can also be understood on the present model by using reactions such as (10) and (11), where reaction (11) is



the rate-determining step. When basic aprotic solvents are added, the concentration of (OH)_{free} groups fall but that of (LP)_{free} groups rises, and these changes nearly compensate. Thus the rate is largely unaffected.

There are many uncertainties in this highly simplified approach, but if it contains a germ of truth, it may be possible to refine the data to the point of good agreement.

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