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SELECTIVITY AS A MECHANISTIC TOOL IN SOLVOLYTIC REACTIONS.

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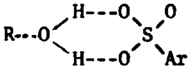
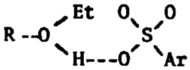
Harris has recently reported that in the solvolysis of adamantyl arenesulphonates, water molecules exhibit greater nucleophilicity than those of ethanol ($k_{ethanol}\ k_{water} < 1$) in an aqueous solution[1]. This inversion in the relative nucleophilic behaviour was attributed to the ability of water to form a double hydrogen bond in the solvent separated ion pair to the two oxygen atoms of the arenesulphonate leaving group (I). This, in contrast to ethanol which cannot form such a structure (II).



(I)



(II)

In support of this proposal it was stated that in the solvolysis of alkyl chlorides where no double hydrogen bond can form, the usual[2] greater nucleophilicity of ethanol was observed. Thus it was concluded that the solvolysis of arenesulphonates produces an inversion in the relative nucleophilicities of ethanol and water, in contrast to the solvolysis of alkyl chlorides which maintains the normal nucleophilic order.

The results listed in Table 1 indicate this interpretation to be incorrect. No account was taken of 1-adamantyl, 2-adamantyl and *exo* 2-norbornyl chlorides, all of which exhibit the same inverse nucleophilicities as the adamantyl arenesulphonates. Furthermore it can be seen that 1-octyl and 2-octyl tosylates as well as benzhydryl p-nitrobenzoate (which should exhibit similar behaviour to the arenesulphonates) are listed with the alkyl chlorides showing the normal nucleophilic order *i.e.* $k_{ethanol} \cdot k_{water} > 1$.

We therefore conclude that it is not the leaving group but the substrate skeleton that

TABLE 1

Relative Nucleophilicity of Ethanol and Water in Solvolysis Reactions in 70% Aqueous Ethanol[a]

Substrates showing $k_E\ k_W > 1$	$k_E\ k_W$	Substrates showing $k_E \cdot k_W < 1$	$k_E : k_W$
p,p'-Dimethylbenzhydryl chloride[b]	18.96	1-Adamantyl chloride[b]	0.576
p-Methylbenzhydryl chloride[b]	7.15	2-Adamantyl chloride[b]	0.169
Benzhydryl chloride[b]	4.91	*exo*-2-Norbornyl chloride[b]	0.843
α-(p-Chlorophenyl)ethyl chloride[b]	2.06	2-Adamantyl tosylate[c]	0.548
α-Phenylethyl chloride[b]	2.08	2-Adamantyl brosylate[c]	0.460
1-Octyl tosylate[d]	1.92	2-Adamantyl benzenesulphonate[c]	0.432
2-Octyl tosylate[d]	1.01		
Benzhydryl p-nitrobenzoate[e]	3.45		

[a] $k_E \cdot k_W$ measures the ratio of the nucleophilicity of ethanol to that of water [b] Result taken from Ref. 1. [c] Result taken from Ref. 4 [d] Data obtained from $k_E\ k_W = \frac{(ROEt)}{(ROH)} \cdot \frac{(EtOH)}{(H_2O)}$. The ratio (ROEt) (ROH) was obtained by glc. [e] Result calculated from data in Ref. 5.

determines the relative nucleophilic order. This may be understood by considering the Winstein solvolysis scheme[3].

$$\begin{tikzcd}
RX \arrow[r, shift left] \arrow[d, "k_1"] & R^+X^- \arrow[l, shift left] \arrow[r, shift left] \arrow[d, "k_2"] & R^+\|X^- \arrow[l, shift left] \arrow[r, shift left] \arrow[d, "k_3"] & R^+ + X^- \arrow[l, shift left] \arrow[d, "k_4"] \\
P & P & P & P
\end{tikzcd}$$

Substrates that cannot undergo backside nucleophilic substitution and which do not readily form stable carbonium ions, have only k_3 available as the major product determining route, since k_1 and k_2 involve backside attack and k_4 depends on the formation of a free carbonium ion. The substrates in Table 1 which fall into this category are the adamantyl and norbornyl derivatives, the very compounds which show inverse selectivity Thus it appears that water is a stronger nucleophile than ethanol in the k_3 product determining step This effect is presumably due to a greater stability of the water separated ion pair combined with the fact that formation of the solvent separated ion pair is essentially irreversible. This would give rise to the greater formation of alcohol product and the apparent greater nucleophilicity of water. The reason for the greater stability of the water separated ion pair may stem from two possible causes a) a water molecule, being less bulky than an ethanol molecule , more readily interposes itself between the two ions of the intimate ion pair, b) water, being more acidic, more readily stabilises the leaving group through a more effective hydrogen bond.

For the product determining steps, k_1, k_2 and k_4, the normal order of nucleophilicities of ethanol and water is expected to hold. As a consequence, for substrates able to undergo product formation by several or all of the routes k_1 to k_4 , the relative nucleophilicities of ethanol and water, or more quantitatively, the selectivity of nucleophilic attack k_E k_W is expected to be the weighed average of the selectivity of attack of each of four rate determining steps. Since this weighed average is expected to favour ethanol as the better nucleophile, it is not surprising to observe that in aqueous ethanol solvolyses, ethanol is, in fact, generally found to be more nucleophilic than water

In conclusion it can be seen that selectivity studies may be used as a highly subtle tool in the elucidation of solvolytic reaction mechanism and further work to extend the capabilities of this technique are now in progress.

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