A STABILITY-SELECTIVITY RELATIONSHIP FOR REACTION OF ALKYL CHLORIDES IN A BINARY, NUCLEOPHILIC SOLVENT

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We have previously shown that a stability-selectivity relationship exists for the solvolysi of p-substituted 2-adamantyl arenesulfonates in which the two competing pathways are attack by nucleophiles ethanol and water on an intermediate ion pair, eq. 1.[1] The observed relationship

$$R-X \longrightarrow \ulcorner Inter \urcorner \begin{cases} \xrightarrow{EtOH} ROEt \\ \xrightarrow{H_2O} ROH \end{cases} \quad (1)$$
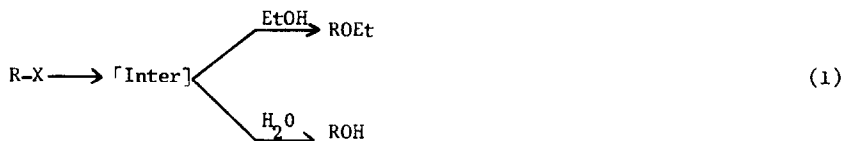
showed that an increase in stability resulted in an increase in the ROH/ROEt product ratio. This apparent greater nucleophilicity of water was interpreted as evidence that products are derived from nucleophilic attack on or collapse of I and II, and as evidence that increasing stability of the ion pair increases the relative amounts of I to II. A structure such as I cannot obtain for

I   II
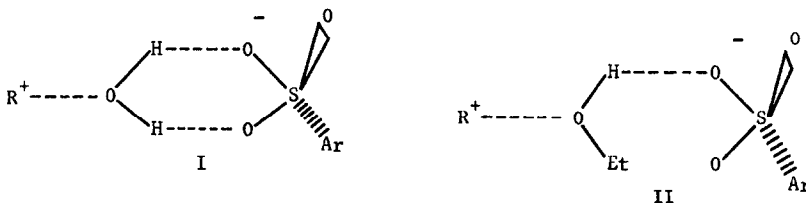
alkyl-chloride ion pairs. Thus if the above postulate for 2-adamantyl arenesulfonates is correct, alkyl chloride solvolysis should give a decrease in the ROH/ROEt product ratio with an increase in ion pair stability; i.e., the usual[2] greater nucleophilicity of ethanol relative to water would be shown.

We have studied the nature of the relationship between stability and selectivity for the aqueous ethanolysis of a series of alkyl chlorides which are also believed to react via solvent separated ion pairs.[3-5] The necessary kinetic and product information are given in Table 1. We have used the log of the solvolysis rate in aqueous acetone as a measure of stability of the intermediates. The use of log $\underline{k}$ in this manner will introduce some error because of possible ion pair return, solvation differences, and nonlinearity between reactivity and stability,[6] but the rate variation of 10^{11} for the compounds studied is sufficient to minimize these effects.

A fair linear correlation is obtained between log $\underline{k}$ (stability) and log $\underline{k}_E/\underline{k}_W$ (selectivity) Figure 1, with only one point (p,p$'$-dichlorobenzhydryl) deviating significantly from the linear correlation. Possibly, this deviation results from selective solvation about the intermediate ion pair. The positive slope obtained for the alkyl halides is in direct contrast to that for the 2-adamantyl arenesulfonates, and thus is consistent with our proposal that the negative slope results because of the greater stability of I relative to II.

Table 1. Rates and products for the solvolysis of a series of alkyl chlorides in 70%(v/v) ethanol.

Chloride	$\underline{k}$ (sec^{-1}) (25°) (80% acetone)[a]	ROEt/ROH[b] (70% ethanol)[a]	log $\underline{k}_E/\underline{k}_W$[c]
p,p$'$-Dimethylbenzhydryl[d]	2.70×10^{-2}	13.5 ± 2.9 (25°)	1.04
p-Methylbenzhydryl	1.57×10^{-3}	5.09 ± 0.62 (25°)	0.84
Benzhydryl[d]	7.25×10^{-5}	3.5 ± 0.1 (25°)	0.70
p-Chlorobenzhydryl[d]	2.31×10^{-5}	5.8 ± 0.3 (25°)	0.90
α-Phenylethyl	6.08×10^{-7}	1.48 ± 0.02 (50°)	0.31
α-(p-Chlorophenyl)ethyl	1.81×10^{-7}	1.47 ± 0.05 (50°)	0.31
p,p$'$-Dichlorobenzhydryl	1.45×10^{-5}	0.550 ± 0.078 (75°)	-0.35
exo-2-Norbornyl[d]	7.00×10^{-9}	0.60 ± 0.01 (100,125,150°)	-0.079
1-Adamantyl[d]	1.10×10^{-9}	0.41 ± 0.01 (100,125,150°)	-0.25
2-Adamantyl[d]	5.30×10^{-13}	0.12 ± 0.01 (200°)	-0.80

[a] Volume percent in water. [b] Determined by vpc and the result of five or more measurement. Substrate was 0.01 M with 0.012M pyridine. [c] Derived from $\dfrac{k_E[C_2H_5OH]}{k_W[H_2O]} = \dfrac{ROEt}{ROH}$. [d] Rate taken from D. J. Raber, J. M. Harris, R. E. Hall, and P. v. R. Schleyer, J. Amer. Chem. Soc., 93, 4821 (1971).

Thus it seems clear that the insulating molecule in a solvent separated ion pair can act as a nucleophile, and that reaction by this pathway will lead to products with retention of stereochemistry.
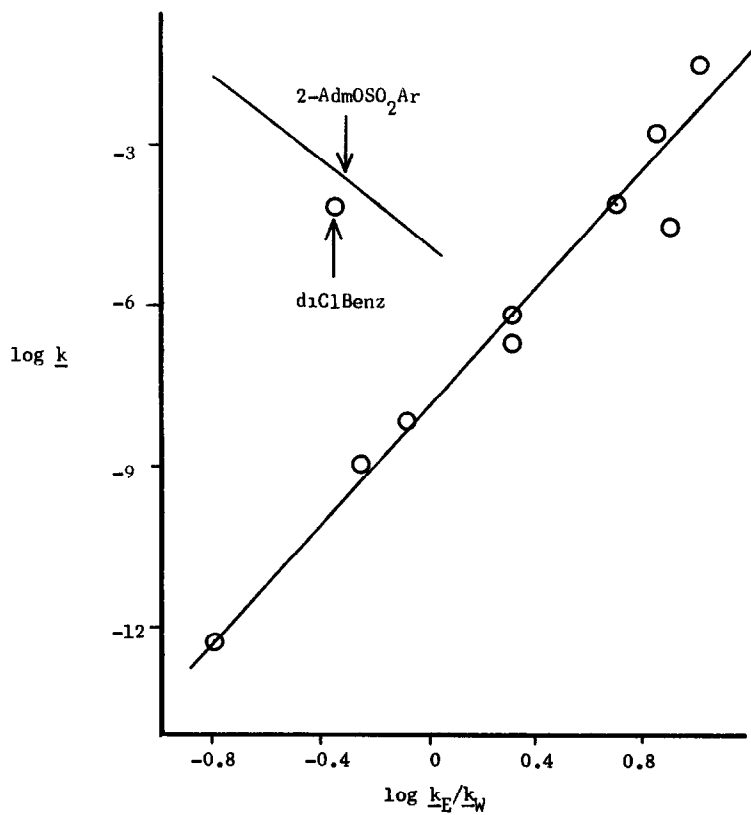

Figure 1. Log $\underline{k}$ vs. log $\underline{k}_E/\underline{k}_W$ for 2-adamantyl arenesulfonates[1] and alkyl chlorides in 70%(v/v) aq. ethanol.

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