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REACTIVITY-SELECTIVITY RELATIONSHIPS. III.[1]
EVIDENCE FOR ION PAIR INTERMEDIATES IN THE SOLVOLYSIS OF SECONDARY DERIVATIVES

Addy Pross* and Rodi Koren
Department of Chemistry, Ben-Gurion University of the Negev,
Beer-Sheva, Israel

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The possible formation of ion pairs in S_N2 type solvolysis reactions was first proposed by Sneen[2] and coworkers. The suggested solvolysis scheme which may be written:

$$RX \rightleftharpoons R^{+} X^{-} \rightarrow ROS$$

has since been supported by Scott[3] and Koskikallio[4].

We wish to present evidence which supports the Sneen ion pair mechanism for poor nucleophiles but strongly indicates that with powerful nucleophiles a traditional,concerted S_N2 reaction takes place. The experimental data is listed in Table 1.

A number of 2-octyl derivatives were solvolysed in different aqueous ethanol solutions and the product distribution of the resulting 2-octyl ethyl ether and 2-octanol established by response calibrated g.l.c. From the product distribution, the selectivity of attack of ethanol and water in the product determining step was determined. The data in Table 1 show that all the 2-octyl derivatives studied in the various aqueous ethanol mixtures show essentially no selectivity whatever. This result suggests that attack of solvent takes place on some highly reactive species whose rate of reaction approaches a value which is diffusion controlled. Clearly, such an active species is more consistent with an ion pair intermediate than with the neutral substrate

An interesting point however, is that this behaviour is quite different in the presence of a strong nucleophile such as azide ion. We have compared the available selectivity data for a

Table 1: Selectivity[a] data for the solvolysis of 2-octyl derivatives

Solvent % (V/V) ethanol	Substrate: 2-Octyl X			
	X=Chloride	X=Bromide	X=Tosylate	X=Brosylate
95	0.7 ± 0.1	0.7 ± 0.1	0.7 ± 0.1	0.7 ± 0.1
90	0.8 ± 0.1	0.8 ± 0.1	0.7 ± 0.1	0.8 ± 0.1
70	1.1 ± 0.1	1.0 ± 0.1	0.8 ± 0.1	0.9 ± 0.1
50	1.1 ± 0.1	1.1 ± 0.1	0.9 ± 0.1	1.2 ± 0.3

[a] Selectivity was defined as $k_{ethanol}:k_{water}$ and determined from $\frac{[\text{octyl ether}]}{[\text{octyl alcohol}]} : \frac{[\text{ethanol}]}{[\text{water}]}$

All product data were obtained by g.l.c. and represented the average of at least 3 determinations on duplicate runs.

number of alkyl chlorides, which solvolyse via ion pair intermediates using two different selectivity parameters; one based on the competition between ethanol and water[5], the other between azide ion and water[6]. The graph in Figure 1 shows the selectivity values obtained by the two methods, plotted against each other. With the exception of the 2-octyl substrate a good correlation of unit slope is obtained. This correlation of two independent measures of selectivity is of considerable significance since it lends support to the view that selectivity values do reflect the ability of a species to discriminate between different reagents. The position of 2-octyl chlori however falls wide of the line. This means that the selectivity of 2-octyl chloride is considerably <u>less</u> than that for substituted benzhydryl derivatives using the competing nucleophiles ethanol and water, while with the competing nucleophilic system,azide ion and water, 2-octyl chloride shows far <u>greater</u> selectivity. This result, we feel, indicates that a different mechanism operates for the solvolysis of 2-octyl derivatives in the two different systems. In aqueous ethanol, where no strong nucleophile is present the selectivity data indicates the intermediacy of a highly reactive ion pair For the azide ion in aqueous solution, the high selectivity indicates that attack of azide ion on neutral substrate is much prefered to that of water, leading to the high selectivity observed. This interpretation, of course, does not rule out the possibility of attack on the ion pair in the azide solution. It merely suggests that product formation will be predominantly via attack on

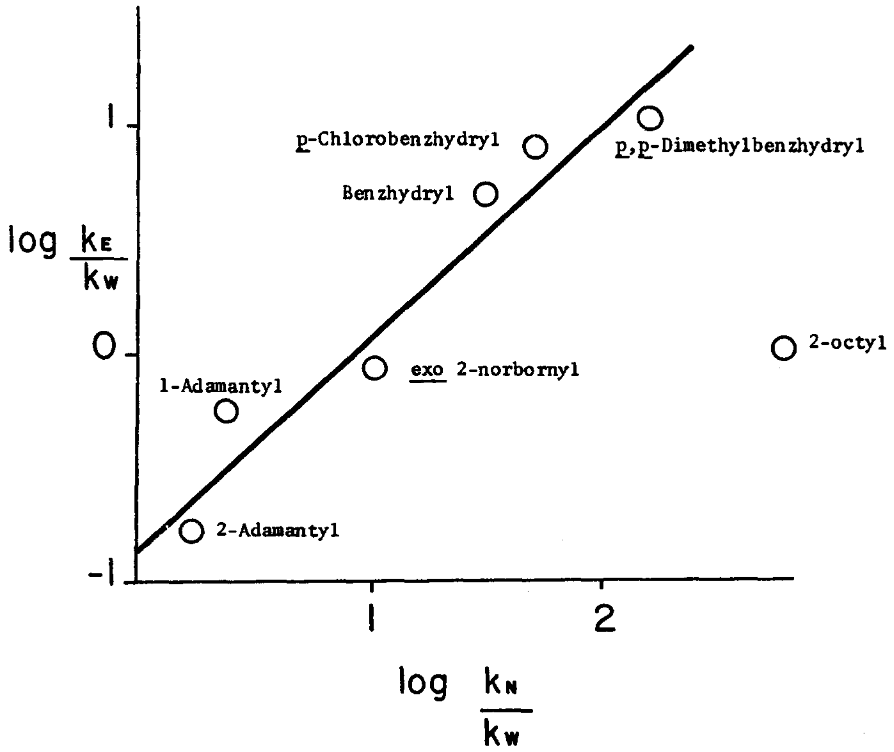

Figure 1: A plot of selectivity based on the competition between ethanol and water in 70% aqueous ethanol against the selectivity based on competition between azide ion and water for a number of alkyl chlorides.

neutral substrate. In aqueous ethanol solution where no strong nucleophile is present, solvolysis takes place after initial activation of the substrate by solvent assisted ion pair formation.[7]

The conclusions reached in this communication are based on application of the reactivity-selectivity principle.[8] It is true that recently some workers have questioned the validity of the principle[9,10], *i.e.* that a small reduction in the reactivity of a species will lead to a corresponding increase in its selectivity. However, as Kemp[9] has pointed out, in the limit the principle must be valid. That is, if the reactivity of a species is increased to a level where its reactions are essentially diffusion controlled the selectivity will drop to a value close to zero (defining selectivity as log k_1/k_2). The selectivity values obtained in this study suggest in fact, that this is the reactivity range studied.

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