Evidence for Ion Pair Intermediates in the Solvolysis of Primary and Substituted Benzyl Derivatives[1]

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Summary Application of the reactivity–selectivity principle indicates the existence of ion pairs in the solvolysis of a primary system.

THE question of ion pair intermediates in the solvolysis of primary and secondary substrates remains one of considerable controversy, because it has proved exceedingly difficult to distinguish between a mechanism involving ion pairs and one involving direct substitution on neutral substrate.[2,3]

We have utilized selectivity studies† in the examination of a primary system to provide what we consider to be a clear-cut distinction between these two possibilities. This is achieved by investigating the nature and stability of the species undergoing attack in the product determining step. The conclusions are based on application of the reactivity–selectivity principle[4] which relates the selectivity of a species to its reactivity within a closely related family. Highly reactive species are generally unselective in their reactions while unreactive species exhibit high selectivity.‡ We have studied the aqueous ethanolysis of octyl and benzyl derivatives in this way and compared the results with available data for benzhydryl *p*-nitrobenzoate.[6]

TABLE

Selectivity[a] of octyl derivatives (Oct X).

Substrate Oct X	% (v/v) ethanol					
X	50	60	70	80	90	95
Cl	1·97	1·74	1·53	1·32	1·06	0·97
Br	1·78	1·59	1·46	1·27	1·03	0·89
p-MeC$_6$H$_4$SO$_3$ . .	1·82	1·57	1·51	1·27	1·04	0·93

[a] Selectivity defined as $k_E:k_W$ and determined from ([octyl ether]/[octyl alcohol]) : ([EtOH]/[H_2O]). All product data from which the selectivity data were derived were obtained by at least 3 determinations on 2 or more runs using response-calibrated g.l.c. Maximum error in selectivity data is estimated at 5%. Solvolyses were conducted at 120 °C in the presence of excess of lutidine.

Our results provide four separate proofs that ion pairs are involved in the aqueous ethanolysis of octyl derivatives:

(i) The most striking result is that octyl chloride, bromide, and tosylate all exhibit extremely low selectivity toward attack by ethanol and water.§ The data in the Table indicate that the selectivity values for these octyl sub-

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† Selectivity is defined as k_E/k_W where k_E and k_W are the rate constants for the reaction of the species with ethanol and water respectively.

‡ It should be noted that the reactivity–selectivity principle is not universally valid [ref. 4(b); C. D. Johnson, *Chem. Rev.*, 1975, **75**, 755]. Cation–anion combination reactions have been found to violate the principle (C. D. Ritchie, *Accounts Chem. Res.*, 1972, **5**, 348). This breakdown has been attributed to the dominant influence of solvent (A. Pross, *J. Amer. Chem. Soc.*, 1976, **98**, 776). For the closely related solvolytic reactions, however, Schleyer (D. J. Raber, J. M. Harris, R. E. Hall, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, 1971, **93**, 4821) and Harris *et al.* (ref. 5) have shown that reactivity and selectivity do correlate. Apparently for these reactions bond making and breaking contribute significantly to the free energy of activation over and above the effect of solvation.

§ This is analogous to 1-methylheptyl derivatives which also exhibit very low selectivity (ref. 1). However, the conclusion that 1-methylheptyl derivatives are solvolysed *via* the intermediate formation of ion pairs is less remarkable since secondary derivatives are classified as 'borderline' in their solvolytic behaviour because they exhibit features intermediate between limiting S_N1 and S_N2 (refs. 2 and 3).

strates range from 1·97 in the more aqueous solutions to *ca.* 1 in the less aqueous solutions. By comparison, the highly reactive intermediates formed in the aqueous ethanolysis of benzhydryl derivatives yield selectivity values of up to 11.[5] These solvolytic intermediates are many orders of magnitude more reactive than neutral octyl substrates, and yet they exhibit substantial selectivity. The very low selectivity values observed for octyl derivatives suggest therefore that the product-determining step is not attack on a neutral substrate but takes place on a highly active species which exhibits low discriminating ability. We suggest this species is the ion pair.

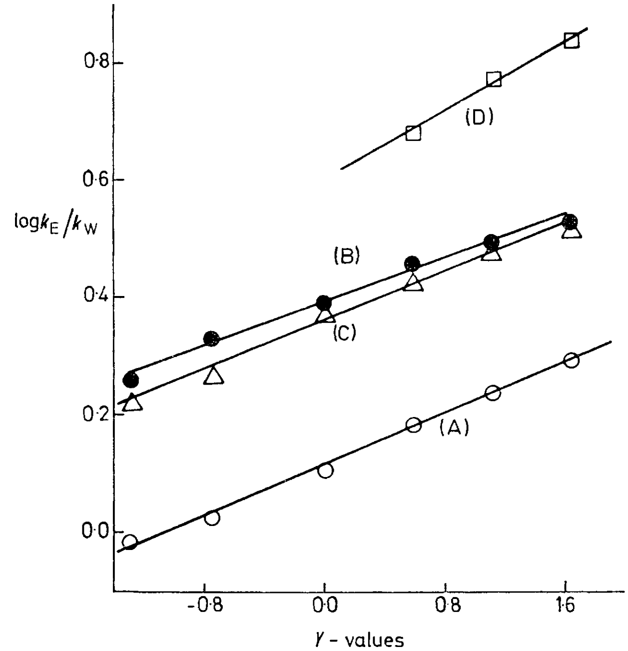

FIGURE. Plot of the logarithm of selectivity against solvent ionizing power (Y-values) for (A) octyl, (B) benzyl, and (C) *p*-chlorobenzyl chlorides and (D) benzyhdryl *p*-nitrobenzoate.

(ii) There is no significant leaving group effect on selectivity as indicated in the Table; this, despite the significant reactivity range covered (the tosylate–chloride leaving group ability in S_N2 reactions is *ca.* 200 : 1[7]). In contrast, the selectivity of benzhydryl[8] and trityl[9] derivatives do show a dependence on the leaving group. This is attributed to the variation in the stability of the possible ion pair intermediates. As we have mentioned earlier, these solvolytic intermediates are highly reactive in comparison to neutral octyl substrates and it is therefore difficult to comprehend why competitive attack on various octyl derivatives would not also exhibit significantly different selectivities. We are again led to conclude that attack takes place on the highly active ion pair which shows very low discriminating ability and which is therefore not materially affected by variations in the leaving group.

(iii) A plot of the logarithm of selectivity of octyl, benzyl, and *p*-chlorobenzyl chlorides as a function of solvent ionizing power (Figure) gives rise to linear correlations (correlation coefficients 0·999, 0·993, and 0·996 respectively) in which all compounds show greater selectivity in the more aqueous solution. This may be understood if the product-determining step operates on a species in which considerable charge development has taken place, a result which is also consistent with the intermediacy of an ion pair. This is because an increase in solvent polarity is expected to stabilize the resultant ion pair leading to greater selectivity.

(iv) The observed selectivity order for the four substrates shown in the Figure corresponds to the relative ability of the four systems to stabilize a species possessing substantial cationic character. Thus the benzhydryl system shows greater selectivity than the benzyl and *p*-chlorobenzyl systems which in turn show greater selectivity than the octyl system. This cationic character is also indicative of an ion pair intermediate.

These data are inconsistent with a concerted S_N2 reaction and lead us to conclude that a nucleophilically solvated ion pair is formed in the aqueous ethanolysis of octyl substrates.

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