ION PAIRING IN 2-ADAMANTYL ARENESULFONATE SOLVOLYSIS: A STABILITY-SELECTIVITY PROBE

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The mechanism of solvolysis of 2-adamantyl derivatives is of current interest because of its

critical relationship to the mechanism of "borderline" solvolysis.[1-4] Schleyer and his coworkers[1]

have shown that 2-adamantyl derivatives, unlike most unstabilized secondary substrates, solvolyze

without nucleophilic solvent assistance, and have used this molecule as a reference system to

determine the extent of nucleophilic solvent assistance in other substrates. The mechanism of

2-adamantyl solvolysis was further specified when Shiner and Fisher[2] found that the γ-deuterium

isotope effect for 2-adamantyl tresylate (2,2,2-trifluoroethylsulfonate) solvolysis was a maximum

value (1.22 for sulfonates) and was independent of solvent. On this basis these workers concluded

that the rate limiting step for 2-adamantyl solvolysis is conversion of tight ion pair into solvent

separated ion pair. Product formation presumably results from nucleophilic attack on the solvent

separated ion pair.

We have tested the possibility of ion pairing and the nature of the product-determining step

in 2-adamantyl arenesulfonate (I) solvolysis by varying the arenesulfonate leaving groups and

determining product ratios in a binary solvent (ethanol-water). If the products are determined by

nucleophilic attack on an ion pair, the leaving group will affect the product ratio. Furthermore,

a relationship should exist between the stability of the ion pair and the selectivity of its

destruction by ethanol or water.[5] The kinetic and product information necessary to test this

postulate are given in Table I.

A stability-selectivity relationship is observed (Fig. 1) and it must be concluded on this

basis that 2-adamantyl arenesulfonates solvolyze not by formation of a classical cation but by

formation of an ion pair, followed by nucleophilic attack on this ion pair to give products.

Table 1. Rates and Products for 2-Adamantyl-p-X-benzenesulfonates in 70%(v/v) Ethanol.

X	T(^{o}C)	k($\times 10^4$ sec^{-1})[a]	ROH/ROEt[b]	log k_E/k_W[d]
$-OCH_3$	100.2	5.79 ± 0.19	1.94	−0.15
	75.8	0.472 ± 0.010		
	75[c]	0.433		
$-CH_3$	100.3	7.94 ± 0.01	2.56	−0.27
	75.8	0.621 ± 0.010		
	75[c]	0.570		
$-H$	75.4	13.5 ± 0.1	3.25	−0.37
	75.8	1.07 ± 0.01		
	75[c]	0.985		
$-Br$	75.6	36.6 ± 0.3	3.05	−0.34
	75.8	3.39 ± 0.01		
	75[c]	3.13		
$-NO_2$	76.2	23.6 ± 0.3	5.20	−0.58
	50.9	0.733 ± 0.05		
	75[c]	20.3		

[a] Determined conductimetrically. [b] Determined by vpc and accurate within 5%. Solvolysis was performed at 100°C for approximately ten half lives, and all products were shown to be stable. Substrate concentrations were 0.01M. [c] Calculated. [d] From $\dfrac{k_E[C_2H_5OH]}{k_W[H_2O]} = \dfrac{ROEt}{ROH}$
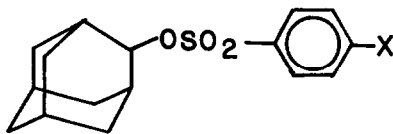
$$X = -OCH_3, -CH_3, -H, -Br, \text{ and } -NO_2$$

I

One unusual aspect of this relationship is the apparent greater nucleophilicity of water as compared to ethanol; as the stability of the ion pair increases, ROH/ROEt increases.[6] For most substrates ethanol is more nucleophilic than water.[6-8] The bias of the 2-adamantyl arenesulfonate ion pairs for water over ethanol is consistent with the product forming step as nucleophilic attack

on a solvent separated ion pair or collapse of this ion pair. A solvent separated ion pair might be expected to favor "incorporation" of water rather than ethanol because of the possibility for formation of two hydrogen bonds with water (II and III). In view of our earlier observation of a positive slope for less reactive alkyl halides[6] and the negative slope observed for I, it seems quite likely that the slope of the stability-selectivity plot in a binary, nucleophilic solvent may be diagnostic for the type of ion pair involved in the product determining step.

II   III

The interpretation of the product-determining step as nucleophilic attack on a solvent separated ion pair or collapse of this ion pair is also consistent with the observation of Bone and Whiting[3] that 2-adamantyl derivatives solvolyze with excess retention of configuration since this ion pair should favor frontside entry of solvent nucleophile.[2,9,10] It is critical to note that our interpretation obviates the necessity for postulating nonclassical ion formation to account for retention of configuration upon solvolysis if it can be shown that a solvent separated ion pair is involved. Whether or not such an occurrence can account for complete or only partial retention of configuration will be the subject of future investigations.
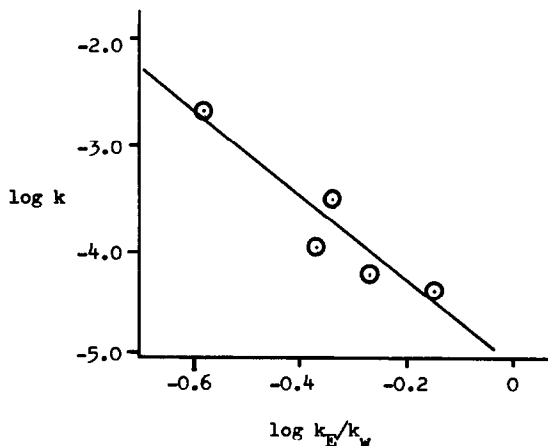

Figure 1. Stability-Selectivity Plot for Cationoid Species Derived from Solvolysis of Alkyl 2-Adamantyl Arenesulfonates.

References

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