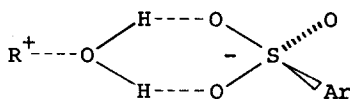# SELECTIVITY IN SOLVOLYSIS OF 1- AND 2-ADAMANTYL
ARENESULFONATES AND BROMIDES IN ETHANOL-2,2,2-TRIFLUOROETHANOL
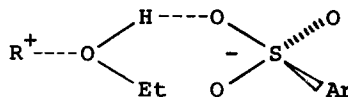
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The character and the role of ion-pairs have been one of the main subjects of recent studies on ionic reactions.[1,2] Harris and his collaborators studied solvolysis of a series of 2-adamantyl arenesulfonates in a binary solvent, ethanol-water, and observed a stability-selectivity relationship in the region of negative selectivities ($k_{ethanol}/k_{water} = k_E/k_W < 1$), where water molecules look like to exhibit greater nucleophilicity than those of ethanol molecules.[3] They attributed these phenomena to the ability of water to form a double hydrogen bond with two oxygen atoms of an arenesulfonate leaving group in a solvent separated ion-pair (1). Ethanol, on the contrary, can not adopt such a structure (2).

This interpretation was opposed by Pross on the basis that even 1- and 2-adamantyl chloride, and *exo*-2-norbornyl chloride, to which no such double hydrogen bond could be expected, showed negative selectivities.[4,5] He claimed that the apparent greater nucleophilicity of water must result from the greater stability of the water separated ion-pair, which, in turn, may stem from two possible causes: a) the less bulkiness of a water molecule than an ethanol molecule, and b) the higher acidity of water.

It is difficult to decide the relative importance of the three factors Harris *et al*. and Pross proposed, because the water separated ion-pair can be more stable than the ethanol separated ion-pair by every factor of them. In order to simplify the situation, we have investigated selectivities in another binary solvent system, 50%(v/v) ethanol-2,2,2-trifluoroethanol.

Both of ethanol and water have high nucleophilicity and similar acidity. Water is much less bulkier than ethanol, and the dielectric contant of water

is much larger than that of ethanol. As a consequence, the difference in
ionizing power between these two solvents are quite large. On the other hand,
the dielectric constant of trifluoroethanol is almost the same as that of
ethanol. Trifluoroethanol is slightly bulkier than ethanol, but the difference
is not so extreme as ethanol-water. Both of the two alcohols are monofunctional
but differ significantly in nucleophilicity and electrophilicity (or acidity).[6]
Therefore, comparison of selectivities in these two binary solvents should
have given valuable information on the factors determining selectivities.

Rate constants were determined titrimetrically in the presence or absence
of 1.1 molar equivalents of 2,6-lutidine. Analysis of reaction products
after more than 15 half-lives was performed by gas chromatography. The
products, adamantyl ethyl ethers (ROEt) and adamantyl trifluoroethyl ethers
(ROTFE), are stable to the reaction conditions in the presence of 2,6-lutidine.
Selectivities (k_E/k_T) were calculated by use of eq 1. Results are summarized
in Table 1.

$$\frac{k_E}{k_T} = \frac{[ROEt]}{[ROTFE]} \times \frac{[CF_3CH_2OH]}{[C_2H_5OH]} \qquad (1)$$

It is apparent from Table 1 that the selectivities did not vary widely
and were close to unity for all substrates employed. Especially, the
substituents on the benzenesulfonate leaving group had no effect on the
selectivities of both the 1- and 2-adamantyl esters. It is important that
negative selectivities ($k_E/k_T < 1$) were observed for most cases studied in
this binary solvent.

Constant selectivities independent of the arenesulfonate leaving groups
might be considered as the evidence that the reaction proceeds *via* the free
carbonium ion. However, it is highly unlikely for an unstabilized, secondary
cation such as 2-adamantyl in not so a limiting solvent of 50% ethanol-
trifluoroethanol ($N = -0.63$ and $Y = -0.59$).[6] On the other hand, the possibility
of the formation of highly unstable cationic species without the ability of
discrimination can be denied based on the inherent selectivities for each of
two series of arenesulfonates and two bromides.

From these facts and the necessity of the structure of adamantane,
products must be formed by front-side collapse of solvent separated ion-pairs
exclusively in the 1-adamantyl system and mainly in the 2-adamantyl system.[7]
Therefore, the negative selectivity close to unity must reflect the relative
stability of the intermediates, the trifluoroethanol separated ion-pair *vs*.
the ethanol separated ion-pair.

Among the properties of the two alcohols described above, nucleophilicity
and bulkiness favor ethanol, functionality is same for the both alcohols,
and only acidity is the factor favoring trifluoroethanol and causing the
negative selectivity. Consequently, the results obtained here verified that

Table 1.   Solvolysis Rates and Products in 50%(v/v) Ethanol-trifluoroethanol

Substrate	$T/°C$	$10^5 k/s^{-1}$ [a]	$T/°C$	ROEt/ROTFE [b]	k_E/k_T [c]
[2-Adamantyl p-X-Benzenesulfonates]					
X = CH_3O	80	1.52±0.01	90	0.909±0.003[d]	0.738
CH_3	80	2.16±0.01	90	0.908±0.003[d]	0.737
H	80	3.57±0.02	90	0.910±0.005[e]	0.739
Br	80	8.50±0.06	90	0.955±0.013[e]	0.775
NO_2	45	0.778±0.003	90	0.962±0.002[d]	0.781
	65	8.87±0.04			
	80	45.9[f]			
[1-Adamantyl p-X-Benzenesulfonates]					
X = CH_3O	25	(2.73)[g]	25	0.707±0.002[e]	0.575
CH_3	25	(4.40)[g]	25	0.706±0.002[e]	0.574
Cl	25	(22.8)[g]	25	0.727±0.001[e]	0.590
[Adamantyl Bromides]					
2-Adamantyl	75	0.00824[f]	135	1.36±0.01[e]	1.11
	135	1.55±0.05[h]	155	1.48±0.01[e]	1.20
	155	6.44±0.24[h]			
1-Adamantyl	75	8.63[i]	75	0.829±0.007[e]	0.674
			90	0.844±0.003[d]	0.685

a) Rate constants are average values of duplicate or triplicate runs.
Substrate concentrations were 0.02 M.   For solvolysis of the bromides,
0.022 M of 2,6-lutidine was added.   Reactions exhibited good first-order
kinetics with correlation coefficients greater than 0.999 over two half-lives
and with a reproducibility of ±2% unless otherwise stated.   b) Relative
yields were sensitivity-corrected.   Substrate concentrations were 0.02 M,
and 0.022 M of 2,6-lutidine was added.   Concentrations of the lutidine had
no effect on the relative yields.   c) Calculated by use of eq 1.   d) Average
values of six or more measurements for single runs.   e) Average values of
duplicate or triplicate runs.   f) Calculated from data at other temperatures.
g) Rate constants in abs. ethanol taken from ref. 8.   h) Calculated infinity
titers were employed to improve the rate plots, but the results were still
worse than other cases.   Similar observations were reported in solvolysis
of 1-haloadamantanes.[9]   i) Rate constant of a single run.

electrophilic solvation through hydrogen bonding to the anionic part of the
solvent separated ion-pair is important for its stabilization.

On the other hand, the negative selectivities observed in ethanol-water
were more distinct than those in ethanol-trifluoroethanol.[3,5] Apparently,
nucleophilicity and acidity do not contribute much in the former binary
solvent. Bifunctionality, according to Pross, is also a minor factor.
Less bulkiness of a water molecule must be a decisive factor causing the
pronounced negative selectivities in this solvent.

A stability-selectivity relationship observed for 2-adamantyl arene-
sulfonates in ethanol-water[2] and constant selectivities independent of
stabilities in ethanol-trifluoroethanol are difficult to be interpreted
at present. Co-operation and compensation of many factors must have caused
these different results.

In conclusion, electrophilicity and bulkiness of the solvent, both of
which have often been overlooked, are important factors determining the
selectivity in a binary solvent, when the solvent separated ion-pair is
involved in the product-determining step. This conclusion is in accord
with a familiar idea concerning the structure of a so-called solvent separated
ion-pair; a cation and an anion insulating a solvent molecule in between.

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