

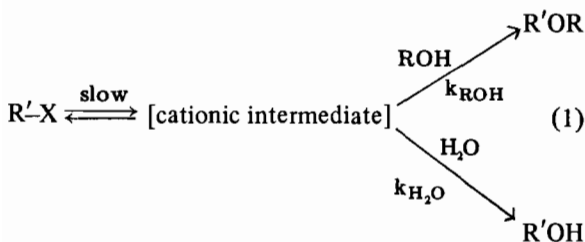
Kinetics and Mechanisms of Organic Chemistry

Solvent–Cationic Intermediate Interactions in Fluorinated Alcohol–Water Systems. Effects on the Selectivity in Solvolysis

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Fluorinated alcohols, pure or in aqueous mixtures, are known to exhibit peculiar solvating properties which are particularly pronounced in the case of hexafluoroisopropyl alcohol (HFP). As a result, unexpected behaviour appear when the effect of such media on the rate of solvolysis is examined. In the present paper we will study the influence of the composition of binary HFP–H₂O systems on solvolysis products, *i.e.* on the selective attack on the cationic intermediate by the two components of the medium.



The results will be compared to those observed in EtOH–H₂O and trifluoroethanol (TFE)–H₂O mixtures (owing to its solvating properties TFE is representative of R_fCH₂OH or R_fCHOHCH₃ fluorinated alcohols). The main purpose of such a study was to determine the various factors which govern the

interactions of a cationic intermediate with these different media.

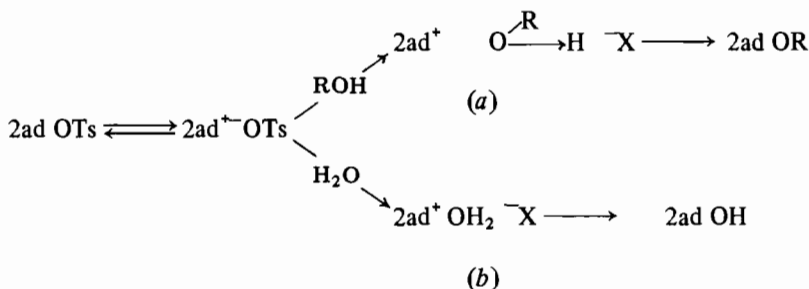
In a solvolytic reaction, like that illustrated in (1), the selectivity is defined by the equation:

$$S = \frac{k_{\text{ROH}}}{k_{\text{H}_2\text{O}}} = \frac{[\text{R}'\text{OR}]}{[\text{R}'\text{OH}]} \frac{[\text{H}_2\text{O}]}{[\text{ROH}]}$$

For a given medium, S can therefore be determined from the relative abundance of reaction products. As in previous studies 2-adamantyl tosylate has been used here as substrate. Owing to its peculiar structure this compound undergoes product formation exclusively via collapse of solvent separated ion pair. Thus the observed variations of the selectivity cannot originate from a change in the nature of the intermediate (as it is generally observed in solvolysis of other substrates) and are directly related to the solvating properties of the medium.

In binary HFP–H₂O systems the selectivity is nearly independent of water content and HFP is always shown to be more efficient than water during the attack on the cationic intermediate. This result appears very surprising since water exhibits considerably higher nucleophilicity than HFP. In this case, the order of 'apparent' nucleophilicity is contrary to the intrinsic nucleophilicity of HFP and water. Such an inversion has already been observed in aqueous ethanol systems, but the latter results appeared much less unexpected due to the small difference in nucleophilicity between EtOH and H₂O. TFE–H₂O mixtures exhibit an entirely different behaviour. In water poor mixtures the selectivity value is in agreement with the intrinsic nucleophilicities (H₂O more efficient than TFE). However the selectivity decreases as the water content increases and an inversion is observed in water rich mixtures.

As a consequence of the mechanism of 2-adamantyl tosylate solvolysis, the selectivity value must



depend, both on the rate of collapse of the solvent separated ion pairs *a* and *b* (relative proton transfer ability of each component of the medium) and on the stability of these ion pairs

The stability of the ion pairs will be mainly related to the following properties of the two components of the solvent (*i*) ability to solvate the leaving group via hydrogen bond, (*ii*) ability to solvate the cationic center, (*iii*) bulkiness of the solvent molecule (which enforces the minimal value of charge separation in the ion pair) The latter factor will be more important in the less dissociating medium We will show how the interactions of the components of the solvent with the cationic center and the leaving group (coupled with their dielectric constant and acidity) account for the selectivity observed in the three considered mixtures and also for its variations with respect to water content

Solvent Effects and Selectivity in Radical Reactions Photochlorination of Arylaliphatics in Pure and Mixed Liquid Phases

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A series of arylaliphatic hydrocarbons (C_6H_5-R with $R = C_2H_5-$, $n-C_3H_7-$, $i-C_3H_7-$, $n-C_4H_9-$, $sec-C_4H_9-$, and $n-C_5H_{11}-$) were submitted to photochlorination in pure and mixed liquid phase The various *mono-chlorination isomers*, generated during the reaction, were separated by G L C, and identified by N M R Kinetics are expressed in terms of relative reactivity, $r r (a/b)$, of a hydrogen (a) versus another one (b), $r r (a/b) = k_a/k_b = R_a/n_a/R_b/n_b$ where R_a and R_b are the observed percentages, and n_a and n_b the number of hydrogens, on each position, a and b [1]

Substitution of hydrogen by chlorine, in the radical chain reaction initiated by light, exclusively takes place in $R-$, and at the same time at the different positions but predominantly in the α position, indicating *selectivity* For instance, pure $C_6H_5-C_2H_5$ gives 90% of $C_6H_5-CHClCH_3$ and 10% of the β isomer, thus $r r (\alpha/\beta) = 13.5$ Indeed chlorinating these pure hydrocarbons, in a temperature range from 20 to 98 °C, differences of activation energies of the chlorination of two hydrogens, H_a and H_b , can be measured The fact is that for ethylbenzene, ($E_a -$

E_b) amounts 3 130 cal mol⁻¹, a value relatively high, accountable for the observed selectivity

On dilution by CCl_4 the selectivity decreases, actually, the relative reactivity varies with the concentration, according to (1)

$$r r (a/b) = \frac{k_{a,o}}{k_{b,o}} + k_{a1}K_1 [C_6H_5-R] \quad (1)$$

including a complexation constant, K_1 , (related to the charge-transfer complex $R-C_6H_5 \cdots Cl^+$), a specific rate, k_{a1} , and a relative reactivity $k_{a,o}/k_{b,o}$ at infinite dilution Equation (1) seems to be valid for $R-$ being C_2H_5- , $n-C_3H_7-$, $i-C_3H_7-$, $sec-C_4H_9-$ For all the other terms $R = n-C_4H_9-$, $n-C_5H_{11}-$ eqn (2) holds

$$r r (a/b) = \frac{k_{a,o} + k_{a1}K_1 [C_6H_5-R]}{k_{b,o} + k_{b1}K_1 [C_6H_5-R]} \quad (2)$$

with *benzene*, selectivity is enhanced, on the contrary, in the presence of *chlorobenzene* it is depressed The best selectivity is reached with CS_2 , as solvent

All experimental results can be correlated by means of (3)

$$\log r r (a/b) = \rho^*(\Sigma\sigma_a^* - \Sigma\sigma_b^*) + \psi_a + \psi_b \quad (3)$$

accounting for the inductive (σ^*) and mesomeric effects (ψ) of the substituent acting upon the relative reactivity of the $\rightarrow C-H$ bond, the last one (ψ) is only affecting the α position The absolute value of both parameters (ρ and ψ) increases with the concentration of the aromatic substrate in a *suitable solvent* (CCl_4)

One may conclude that *solvents are affecting the intensity of the substituent polar effects* of the substrate and modifying the dipolar characteristics of the transition state of the radical reaction

Reference

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Variations of Solvation Energies of the Protonated Form and the Transition State in the Acid Hydrolysis of Thioamides

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Numerous reactions catalyzed by acids show a rate maximum in moderately concentrated acids