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. (α/β) = 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):

$$\text{r.r.(a/b)} = \frac{k_{a,o}}{k_{b,o}} + k_{a1}K_1\,[C_6H_5\text{–}R] \qquad (1)$$

including a complexation constant, K_1, (related to the charge-transfer complex R–$C_6H_5\cdots Cl^{\bullet}$), 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:

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

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):

$$\log \text{r.r.(a/b)} = \rho^*(\Sigma\sigma_a^* - \Sigma\sigma_b^*) + \psi_a + \psi_b \qquad (3)$$

accounting for the inductive (σ*) and mesomeric effects (ψ) of the substituent acting upon the relative reactivity of the $>$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.

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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

[1]. This maximum would proceed from the decrease of the water activity when the concentration of acid increases. In fact, our study of the hydrolysis of thioamides in aqueous sulphuric solutions, reveals that the origin is only the difference of the variations of solvation energies between the protonated from (XH^+) and the transition state (CT^*). This difference is evaluated by acidity functions. Thioamides were chosen because solvent effects do not exist with aliphatic compounds.

a) *Protonation.* The ^2H (= $-\log h_2$) acidity function [2] governs the protonation of thioamides. This calculated function is almost identical to the experimental functions H_o''' and H_T relative to tertiary amines and thioamides respectively [1, 3]. For a given thioamide, the same pK value is obtained whatever the wavelength in UV spectroscopy and the technical method (UV, ^1H NMR) may be, (pK (thioacetamide) = –2.51; pK (thiobenzamide) = –3.20). The value, $\tau = 2$, of the apparent solvation ratio [2] means that the protonated form gets a solvation energy lower than the one of the oxonium cation ($\rangle C{=}\overset{+}{O}H$, $\tau = 5$) [4], result confirmed by the corresponding values of entropy variations.

b) *Hydrolysis.* By calling H_* (= $-\log h_*$), the acidity function governing the formation equilibrium of the transition state from the neutral form, we demonstrate that the rate law can be written:

$$v = k_o \frac{h_*}{K_*} \frac{|X_o|}{1 + \dfrac{h_{XH^+}}{K_{XH^+}}} \qquad (1)$$

We find that the H_* function is identical to the ^4H function ($^4H \cong H_A$ [1]) and so, the solvation energy of the transition state ($\tau = 4$) is stronger than the one of the protonated form ($\tau = 2$); in effect, we get:

$$H_{XH^+} (= {}^2H) < H_* (= {}^4H) \text{ or } h_{XH^+} > h_* \qquad (2)$$

From the definition of the acidity function and the one of the transfer activity coefficient, this result means:

$$\Delta G_t^\circ (XH^+) < \Delta G_t^\circ (CT^*)$$

where ΔG_t° is the variation of transfert free enthalpy linked to the variation of solvation energy.

In the acidity range, where the inequality $h_{XH^+} \gg K_{XH^+}$ is verified, relation (1) gives:

$$\log k_{exp} = \log \frac{k_o K_{XH^+}}{K_*} + \log \frac{h_*}{h_{XH^+}} \qquad (3)$$

This relation is verified by the experimental values. The rate is decreasing whatever the water activity may be. The rate maximum occurs when the concentration of acid corresponds to the half-neutralization of X. The decrease of the reaction rate proceeds only from the different natures of acidity functions H_* and H_{XH^+}; when the concentration of acid increases the variation of solvation energy of the protonated form is lower than the one of the transition state (inequality (2)).

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Solvation and Reactivity of 2-Adamantyl Tosylate in Fluorinated Alcohol–Water Systems

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Fluorinated alcohols exhibit solvating properties contrary to those of aprotic dipolar solvents. Thus they show a strong solvating ability towards anions (high ionizing power Y) and a weak solvating ability towards cations (low nucleophilicity N). A systematic study of commercial fluorinated alcohols has shown [1] that these properties are particularly pronounced in the case of hexafluoroisopropyl alcohol (HFP) which exhibits *both* the highest ionizing power and the lowest nucleophilicity. The binary mixtures HFP–H_2O possess also peculiar solvating properties; moreover, such media should promote various reactions of synthetic interest and especially cyclization-solvolysis [2].

The above considerations prompted us to examine the effect of water fraction on the ionizing power of HFP–H_2O mixtures, *i.e.* on their ability to promote the heterolytic cleavage of C-leaving group bond during solvolysis. The results will be compared to those observed in EtOH–H_2O and trifluoroethanol (TFE)–H_2O systems (since, as a result of tis characteristics [1], TFE is representative of R_fCH_2-OH and $R_fCHOHCH_3$ fluorinated alcohols).