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

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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)

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

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

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

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)

$$\log r\,r\,(a/b) = \rho^*(\Sigma\sigma^*_a - \Sigma\sigma^*_b) + \psi_a + \psi_b \qquad (3)$$

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

Reference

1 J L Corbiau, J Ph Soumillion et A Bruylants, *Bull Soc Chim Belge*, *79*, 451 (1970)

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