(9) and (10) represent possible alternative reaction steps.

Our results show the first kinetic evidence for an aromatic alkylation involving free carbenium ion. This mechanism can only work in solvents of high polarity and solvating power even in the case of alkylating agents, which are precursors for secondary or tertiary carbocations. The displacement reaction occurs simultaneously as well. In slightly polar media only displacement reaction (6) is operative.

This mechanism change may be due to the polarization of *I* and stabilization of the free cation, both caused by solvent polarity change.

Evaluation of Initial and Transition State Solvation Effects in Aprotic Media by the Competitive Preferential Solvation Theory

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A chemical reaction taking place in aprotic media is frequently submitted also to the influence of specific solvent effects. The problem is even more complicated in mixed aprotic solvents since preferential solvation may contribute to the observed effects. A recently proposed model [1] called the Competitive Preferential Solvation Theory (COPS theory) accounts quite naturally for these phenomena.

Based essentially on five postulates, COPS theory allows the quantitative evaluation of solute–solvent interactions both in initial and transition states. The affinity constants obtained are perfectly transferable and they lead immediately to a new type of linear free energy relationship [2] connecting the interacting power of solvents with their catalytic activity. COPS theory accepts neither 'inert' solvents nor 'free' solutes and it implies a virtual microscopic partitioning in homogeneous media. Beside kinetics COPS theory have been successfully applied to NMR and UV spectroscopies, to nuclear relaxation, to fluorescence proving its general validity.

The kinetic application of COPS theory is illustrated by two reactions (aminolysis of imides and 2 + 4 cycloaddition reaction) in about sixty different media. The results provide a kinetic confirmation of the existence of solvent classes discovered previously [3] in spectroscopy: halogen containing, n-donor and aromatic solvents. All these classes influence differently the chemical reactivity.

No close bonding contacts are apparent between the cation and BPh_4 or CH_3CN.

Upon heating the complex, as a solid or when dissolved in acetonitrile, we observe the loss of ethylene. Reaction of other donor ligands such as PMe_3, CO, O_2.. are investigated and the results will be discussed.

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Differential Ground State and Transition State Stabilization by Dimethylsulfoxide in Ester Hydrolysis by ElcB. Pathway

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Apart from the well documented $B_{AC}2$ mechanism, alkaline hydrolysis of esters also proceeds by the ElcB mechanism which operates in systems having acidic α-H atoms. The differential solvent effects of protic and dipolar aprotic solvents (such as DMSO) on the rate of alkaline hydrolysis of esters have been used as a mechanistic probe to differentiate these two mechanisms [1]. The results of the alkaline hydrolysis of arylphenylacetates(I) and aryl 4-nitrophenylacetates(II) in ethanol–water and DMSO–water systems are presented in this present paper.

For the hydrolysis of I the rate of liberation of phenoxide ion is first order with respect to the ester and the hydroxide ion. The near insensitivity of the rate to change of solvent to $D_2O(k_{H_2O}/k_{D_2O} \approx 1)$ and the high Hammett reaction constant ($\rho = +1.4$) for variation of the leaving group point to the operation of ElcB mechanism. The introduction of a nitro group in the acyl moiety causes instantaneous formation of the carbanion in the case of II. The rate of disappearance of the carbanion is independent of the hydroxide ion concentration in the range employed (0.1–1 *M*). Increasing percentage of DMSO in the solvent increases the rate for both I and II. A comparison of the results of this investigation with those for the hydrolysis of aryl α-phenylmethanesulfonates(III) and aryl α-4-nitrophenylmethanesulfonates(IV) reveals a spectrum of ElcB reactivity [2]. These are rationalised in terms of the relative stabilization of the ground state and transition state by DMSO. Since the transition states are charge extended structures these may well be equally solvated by DMSO. Therefore, any difference in reactivity must stem from the ground state stabilization. The rate retardation in the case of IV had been explained as due to the greater stabilization of the charge extended ground state anion by DMSO. But such an effect is operative to a much smaller extent in the case of II pointing to the relative instability of the carbanion on passing from IV to II. It is shown that I, II and III belong to one group of compounds reacting by ElcB$_{\text{ion-pair}}$ mechanism while IV reacts by the El$_{\text{anion}}$ mechanism in the ElcB spectrum.

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Solvent Effects as a Possible Source of Rate Enhancements in Functional Micellar Catalysis

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Micellar catalysis of functional surfactants has been extensively investigated in recent years [1, 2]. The catalytic properties of micellar surfactants containing the hydroxy, amino, mercapto groups, the imidazole ring and other reactive functions have been mainly tested in the hydrolysis of activated esters and amides [2]. In many cases, large kinetic effects have been observed and some systems come near to enzyme reactions in giving large rate enhancements.

There is large evidence that micellar reactions occur at the micelle–water interface, in the so-called Stern layer. Since the polarity of a micelle is quite different from that of water, submicroscopic solvent effects upon the reaction rates are possible [3]. In the case of surfactants containing anionic reactive functions, the possibility of a reduced hydration of the reactive sites and hence of an increase in the reactivity of the function have been suggested [4].

We report data of a comparative analysis of the esterolytic reactivity of some hydroxy-, mercapto-, and imidazole-functionalized cationic surfactants and of analogous non-surfactant models which indicate that desolvation of the functions and, in general, solvent effects are not a relevant source of rate enhancements. Proximity (concentration) effects and electrostatic factors account for most of the observed catalytic effects of functional (as well as of non functional) [5] micelles.

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Protonation and Solvation in Aqueous Systems of N,N-Dimethylalkylthioamides

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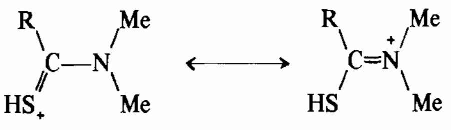
The protonation of N,N-dimethylalkylthioamides in water–sulfuric acid media has been followed through nmr spectroscopy. Bunnett and Olsen treatment of the data gives (for protonation of the methyl derivative at 25 °C) pK = –2.7 and $\phi = -1.1$. The ϕ value suggests protonation at the sulfur atom ($\phi_{\text{sulfides}} = -0.26/-0.35$) rather than at the nitrogen atom ($\phi_{\text{amides}} = +0.42/+0.55$) and wide delocalisation of the charge:



On the other hand, two different N-methyl resonances are observed in water, which collapse into a single resonance upon protonation. This may suggest either a lowering of the rotational barrier upon protonation at nitrogen or protonation at sulfur with collapse of the signals due to a smaller N-methyl resonance difference in the protonated rather than in