vated 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 $ElcB_{ion\text{-}pair}$ mechanism while IV reacts by the El_{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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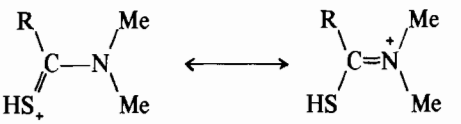
The protonation of N,N-dimethylalkylthioamides in water–sulfuric acid media has been followed through nmr spectroscopy. Bunnett and Olsen treatment of the data gives (for protonation of the methyl derivative at 25 °C) pK = −2.7 and ϕ = −1.1. The ϕ value suggests protonation at the sulfur atom ($\phi_{sulfides}$ = −0.26/−0.35) rather than at the nitrogen atom (ϕ_{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

the free thioamide. Rotational barriers have been calculated as a function of the medium acidity.

Influence of the Solvent on the Anionic Reactivity of Quaternary Onium Salts in Nucleophilic Aliphatic Substitutions. Leaving Group Effects

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Kinetics of nucleophilic substitutions by anions of phosphonium quaternary salts have been measured as a function of the solvent [1, 2], and of the leaving group [3].

$$n\text{-}C_8H_{17}X + Q^+Y^- \xrightarrow[\text{solv.}]{60\ ^\circ C} n\text{-}C_8H_{17}Y + Q^+X^-$$

$Q^+ = C_{16}H_{33}P^+Bu_3$

$Y^- = N_3$, CN, Cl, Br, I, SCN

X^- = Cl, Br, I, Tos, Mes

solv. = MeOH, DMSO, PhCl, cyclohexane.

When the leaving group is a sulphonate ($R-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-O-$; R = Me, Tol), anionic reactivity increases up to 10^3 fold by diminishing the solvent polarity ($k_{MeOH} < k_{DMSO} < k_{PhCl} < k_{cyclo\ hexane}$).

On the contrary, when the leaving group is a halogen (Cl, Br, I) the highest reactivities are found in DMSO and the reactivity scale becomes ($k_{MeOH} < k_{cyclohexane} \leqslant k_{PhCl} < k_{DMSO}$).