

(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 BPh₄ or CH₃CN.

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 PMe₃, CO, O₂.. are investigated and the results will be discussed.

Reference

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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 D₂O($k_{H_2O}/k_{D_2O} \approx 1$) 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 sol-