d'hydratation de la résine. Par ailleurs il a toujours été tenu compte des interactions échangeurs d'ions-solvant [2]. Les points principaux qui ressortent de cette étude peuvent être résumés ainsi:

a) Effectuée en *milieu aqueux* la réaction n'est *pas sélective.*

b) Effectuée en *milieu mixte eau–solvant* le rôle extractant du solvant est mis en évidence et la *réaction devient hautement sélective en dioxanne-1,3.*

c) Effectuée en *milieu organique,* l'eau n'intervenant qu'en quantité très faible et connue dans le sein de la résine, *la sélectivité en dioxanne est maintenue.* Elle est toutefois influencée par les pripriétés du solvant considéré. L'utilisation d'un tel milieu présente surtout l'avantage de mettre en relief de façon très nette les rôles joués par les substituants R,R′ et R″ au niveau de l'activation de la liaison éthylénique.

Les implications de ces divers paramètres, jouant au niveau du soluté et du solvant sur le mécanisme de la réaction sont confirmées par la stéréochimie privilégiée des dioxannes obtenus.

d) Effectuée en *milieu 'non-aqueux'* (résines séchées) l'obtention de dioxannes est très défavorisée au profit de la *formation de polymère* qui devient alors prépondérante.

e) Enfin, il est important de signaler qu'il n'est plus nécessaire d'utiliser le formol en fort excès comme on peut le relever dans la littérature [3, 4]. En effet, dans les conditions qui ressortent de cette étude, l'aldéhyde et l'alcène sont utilisés en *quantités stoechiométriques et conduisent à des réactions quasiment quantitatives.* Ce dernier point met en outre en évidence les avantages que la simplification expérimentale de cette réaction répercutent sur le plan pratique.

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Mechanism Change with Solvent Polarity in Naphthalene Isopropylation

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The kinetics of the naphthalene isopropylation in homogeneous chloro benzene and nitromethane solutions has been investigated using $\mathrm{AlCl_3\cdot CH_3NO_2}$ as catalyst at 25 °C. The rate equations are given by:

$$r_o = k_{obs}[\mathrm{C_{10}H_8}]_o[i\mathrm{PrBr}]_o[\mathrm{AlCl_3\cdot CH_3NO_2}]_o \qquad (1)$$

in chlorobenzene, and

$$r_o = k'_{obs}[\mathrm{C_{10}H_8}]_o^{0.5}[i\mathrm{PrBr}]_o[\mathrm{AlCl_3}]_o \qquad (2)$$

$$= k'[\mathrm{C_{10}H_8}]_o[i\mathrm{PrBr}]_o[\mathrm{AlCl_3}]_o + k''[i\mathrm{PrBr}]_o[\mathrm{AlCl_3}]_o \qquad (3)$$

in nitromethane.

Using other alkyl tromides, the following exponents for $\mathrm{C_{10}H_8}$ have been found in nitromethane:

Alkyl Bromide:	EtBr	*i*PrBr	*t*BuBr	
Exponent of $\mathrm{C_{10}H_8}$:	1.00	0.50	0.39	at −10 °C

In mixed solvents the r_o *vs.* $c_{\mathrm{CH_3NO_2}}$ showed a minima when the ratio $\mathrm{CH_3NO_2{:}AlCl_3}$ ranged between 50 and 100. Due to the $\mathrm{AlCl_3}$ self-ionization, the conductivity of a chloro benzene solution of $\mathrm{AlCl_3\cdot CH_3NO_2}$ increases exponentially with $c_{\mathrm{CH_3NO_2}}$.

Based on these observations and on computing possible reactions, the following mechanisms can be proposed:

in chlorobenzene

$$\mathrm{AlCl_3\cdot CH_3NO_2} + i\mathrm{PrBr} \rightleftharpoons i\mathrm{PrBrAlCl_3} + \mathrm{CH_3NO_2} \qquad (4)$$

$$2\,i\mathrm{PrBrAlCl_3} \rightleftharpoons i\mathrm{PrBr}i\mathrm{Pr^{\cdot +}Al_2Cl_6Br^-} \quad I \qquad (5)$$

$$I + \mathrm{C_{10}H_8} \xrightarrow{\text{slow}} i\mathrm{Pr\text{-}C_{10}H_7} + \text{byproducts} \qquad (6)$$

in nitromethane

$$2\mathrm{AlCl_3} \rightleftharpoons \mathrm{AlCl_2^+\cdot AlCl_4^-} \qquad (7)$$

$$\begin{tikzcd}
\mathrm{AlCl_2^+\cdot AlCl_4^-} + 2i\mathrm{PrBr} \arrow[r, leftrightharpoons] \arrow[d, "\text{slow (9)}", "+i\mathrm{PrBr}"'] & i\mathrm{PrBr}i\mathrm{Pr^+\cdot AlCl_6Br^-} \arrow[dl, "\text{slow (10)}"'] \arrow[d, "\text{slow (11)}"', "+\mathrm{C_{10}H_8}"] \\
i\mathrm{Pr^+} \arrow[r, "\text{fast}", "+\mathrm{C_{10}H_8}"'] & i\mathrm{Pr{-}C_{10}H_7} + \text{byproducts}
\end{tikzcd} \qquad (8)$$

(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 sol-