For each solvent mixture the ionizing power has been determined from Y = log k/k_o where k is the rate constant for solvolysis of 2-adamantyl tosylate in the solvent under examination and k_o that in a reference medium: 80% v/v, ethanol/water. Hence, owing to its peculiar structure 2-adOTs is a suitable substrate for a meaningful determination of ionizing power: 1), the rate determining step is the cleavage of C–OTs bond for an extensive range of solvents including fluorinated alcohols 2), the internal ion pair return is negligible.

In the light of experimental data it can be noted that HFP–H_2O systems appear, at first sight, to exhibit an unexpected behaviour. Although H_2O is considerably more ionizing than HFP, a decrease in the ionizing power of these mixtures is observed as water content increases. Consequently HFP–H_2O systems show a lower ionizing power than each component taken alone.

In sharp contrast, aqueous EtOH mixtures exhibit a 'normal' behaviour, since the ionizing power of the medium increases along with the proportion of water (which is more ionizing than EtOH). However Y always remains below the statistical value according to which $Y_{EtOH-H_2O} = Y_{H_2O}X_{H_2O} + Y_{EtOH}(1 - X_{H_2O})$.

The binary TFE–H_2O mixtures show similar qualitative trend. However, increase in Y with respect to the proportion of water is much less pronounced than in the case of EtOH–H_2O mixtures (though the difference $Y_{H_2O} - Y_{TFE}$ is large). Consequently the ionizing power of the mixture is much lower than the statistical value.

The solvent effects upon the rate of ionization of a substrate such as 2-adOTs mainly depend on the ability of the solvent to interact with the leaving group (OTs) via hydrogen bonding [1]. The hydrogen bonding ability of binary alcohol–water systems arises not only from specific properties of each component, but also from the interactions which appear between their hydrogen bond donor and acceptor sites. We will discuss how the peculiar structure of water ('polymeric' structure involving few donor and acceptor sites) and the structure of alcohols (increase of the donor ability and decrease of the acceptor ability in the following order EtOH, TFE, HFP) account for the whole range of Y variations observed.

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The Role of Solvents on the Behaviour of some Azo Compounds

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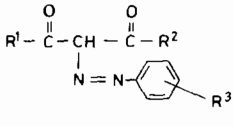
The azo containing groups may behave as +R as well as –R groups, depending on the electronic requirements of the reaction. The aryl azo group is sufficiently polar for proximity effects to become significant in the *ortho* position, where its inherent behaviour may be masked by field effects and by even more interaction with side chain [1]. The β-diketoaryl azo compounds were taken as an example (I). The azo group can act as a proton acceptor in hydrogen bonds and the carbonyl oxygen acts as a proton acceptor with protonic solvents. The sole interaction with acetone will be the hydrogen bonding between the hydrogen of the OH-group and the oxygen of the solvent molecules to decrease the electron density on the oxygen atoms; similar behaviour is apparent in chloroform with slight increase in the strength of the *intra*-molecular hydrogen bonding. The ($^1L_a - {}^1A$) transition of the phenyl ring was solvent independent. The donor *p*-OCH_3 substituent with mesomeric and inductive effects properties, where the electron density on the oxygen atoms of the carbonyl groups assists the electron migration from the highest occupied orbitals of the methoxy group to the vacant orbital on the carbonyl group [2]. The *intra*-molecular hydrogen bonding of the *p*-NO_2 compounos, mainly with π–π* transition of the chromphoric groups is influenced by charge migration from the O–H group, not affected by non polar solvents. The *o*–NO_2 compounds are affected by increasing the volumes of R^1 and R^2. The polar solvent molecules are oriented to the polar sites of the solute in the ground state and on excitation, the solvent molecules are in a position to solvate the more stabilized polar excited states. The non-protonated ligands were the counter part for complexation with divalent transition metals in water–alcohol medium. The stability constants of the traced 1:1 chelates proved that the metals behave as π-electron acceptor depending on the nature of the substituents (σ), the dissociation constants of the ligands (pK) and the nature of the solvent (mainly its dielectric constant) [3].



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Thermodynamic Nitration Rates of Aromatic Compounds from Kinetic Data in Aqueous Sulphuric and Perchloric Acids. A Comparison of the Results Referred to Water as Standard State

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Thermodynamic nitration rates (k_2°) referred to water as standard state are given for some aromatic compounds nitrating *via* Wheland intermediate. The values have been calculated by a new mechanistic criterion (eqn. 1) involving M_C activity coefficient relationship [1–4] (eqn. 2)

$$\log k_2^\circ = \log k_{2_{obs}} - \log[H^+] + \log a_w - \\ - \log K_{HNO_3} - \log \frac{f_{AR} f_{NO_2^+}}{f_{\neq}} - \\ - \log \frac{f_{HNO_3} f_{H^+}}{f_{NO_2^+}} \qquad (1)$$

$$M_C = -\log \frac{f_{B_i} f_{H^+}}{f_{B_iH^+}} \qquad (2)$$

where a_w = water activity, f = molarity activity coefficient and suffixes i, j, *etc.* identify the indicators.

Experimental rate constants (k_{2obs}) measured both in sulphuric and perchloric acids have been used. Thermodynamic pK_a values of nitric acid (equilibria 3 and 4) obtained by Raman spectra in sulphuric [5] and perchloric acids [6] have been also utilized.

$$HNO_3 \rightleftarrows H^+ + NO_3^- \qquad (3)$$

$$HNO_3 + 2HX \rightleftarrows NO_2^+ + H_3O^+ + 2X^- \qquad (4)$$

The validity of the results and the confidence intervals of the values are discussed.

A new nitration scale of reactivity, relative to benzene, is given for some substituted benzene derivatives. Discussions on the rate determining step of benzene are also reported accounting for the results in the range 51–82% H_2SO_4 and 57–65% $HClO_4$ [7].

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Rôle de l'Eau et de la Nature du Solvant sur l'Orientation de la Réaction de Prins

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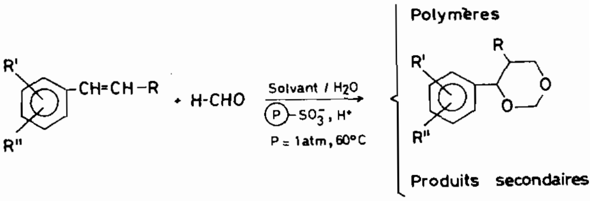
L'étude de la réaction de condensation du formol sous différentes formes (formaldéhyde en solution aqueuse, paraformaldéhyde et trioxanne) sur le styrène et divers substrats présentant le motif styrénique a été réalisée en présence d'un catalyseur acide fort. Ce rôle est ici joué par des résines échangeuses de cations macroporeuses [1].



Des solvants de basicité différentes, des constantes diélectriques variées, miscibles ou non à l'eau ont été choisis pour réaliser ce travail. Ils se sont avérés être pour une grande part *responsables de la haute sélectivité de la réaction en dioxannes-1,3*; l'autre part étant jouée par *l'eau* du milieu réactionnel et

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