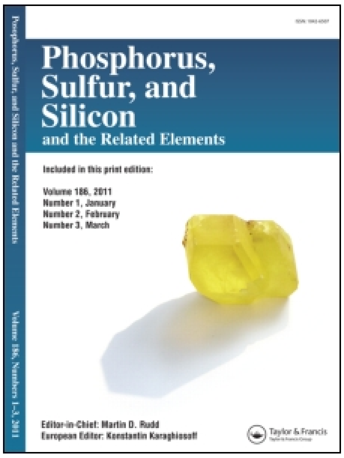

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CATALYTIC EFFECTS IN THE AMINOLYSIS REACTIONS OF ARYLSULPHONIC ACID DERIVATIVES IN NON-AQUEOUS MEDIA

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The catalytic effects of organic bases in reactions of arylamines with arylsulphonic acid derivatives, $ArSO_2X$ (X = Cl, Br, OSO_2Ar) in aprotic media are characterised by the following regularities. 1. The activity of 3- and 4-substituted pyridines, N-alkyl- and N-phenylimidazoles is desribed by the commom Brönsted relationship. Substituents in positions 2 and 2,6 of the pyridine molecule have a strong steric influence. Tertiary cyclic amines of quinuclidine type with the same basicity as pyridines and imidazoles have more higher activity than the latter. N-Oxides of pyridine which are 4-5 pK_a units less basic than the corresponding pyridines have the catalytic activity 100 times as much, as compared with them. 2. The intensity of the catalytic action of pyridines and their N-oxides alters insignificantly with changing the leaving group X in the substrate, somewhat increasing in the order $Cl < Br \leq OSO_2Ar$. 3. The activity of pyridine bases increases with increasing the solvent solvating ability. The inhibiting influence of the X^- anione on the rate of catalytic reaction displays in media of high polarity (nitrobenzene, acetonitrile). These regularities are explained in terms of the nucleophilic mechanism of catalysis which is supported by isolating intermediate adducts of tertiary amines (in particular 4-N,N-dimethylaminopyridine) with arylsulphonic acid bromides and anhydrides and by studies of their reactivity towards arylamines in methylene chloride. Compounds of bifunctional nature (carboxylic acids) do not accelerate the reaction under consideration unlike a similar substitution process at the carbonyl C-atom. The cause of this seems to be a different geometry of transition states in substitution at the sulpho group S-atom and at the carbonyl carbon, respectively.