ABSTRACT

The solvent and structural influences on the kinetics of oxidation of aniline and para- (Me, OMe, COMe, NHCOMe, NO₂, Br, Cl, F) and meta- (Me, OMe, COMe, Et, COOH, NO₂) substituted anilines by two Cr(VI) oxidants viz. imidazolium fluorochromate (IFC) and nicotinium dichromate (NDC) have been carried out in neat organic solvents and in binary solvent mixtures. Electrooxidation of the chosen anilines was investigated in varying mole fractions of binary solvent mixtures with an aim to shed some light on the mechanism of the reaction. The kinetics of aromatic nucleophilic substitution reaction of these anilines with benzenesulphonyl chloride has also been carried out in neat organic solvents and in different binary solvent mixtures of varying compositions. The activation parameters have been computed following the reactions at different temperatures. The influence of structure and solvent on the reactivity has been analyzed using linear and multiple regression equations. The specific and nonspecific solvent-solvent-solute interactions on the reactant/transition state have been separated and quantified using the technique of correlation analysis. Reasons for the difference in reactivity, in all the above reactions, with structural changes in the substrate are also discussed. On the basis of the results of systematic correlation analysis, plausible mechanisms have been proposed for these reactions. The results of this study have been published in reputed journals.