

Effect of Preferential Solvation on the Kinetics and Thermodynamics of Oxidation of Anilines by Nicotinium Dichromate

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The nicotinium dichromate (NDC) oxidation of anilines, in varying mole fractions of benzene/2-methylpropan-2-ol mixtures, in the presence of *p*-toluenesulfonic acid (TsOH) is first order in NDC and TsOH and zero order with respect to anilines in the concentration range investigated. The NDC oxidation of 15 *meta*- and *para*-substituted anilines complies with the isokinetic relationship but not to any of the linear free energy relationships. The activation free energy data failed to correlate with macroscopic solvent parameters such as ϵ_r and E_N^T . Correlation of ΔG^\ddagger with Kamlet-Taft solvatochromic parameters (α , β , π^*) suggests that the specific solute-solvent-solvent interactions play a major role in governing the reactivity.

Key words: Solvent Effect, Aniline Oxidation, Kinetics, Chromium(VI)