



Kinetics and Mechanism of the Oxidation of Some α -Hydroxy Acids by Pyridinium Dichromate

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ABSTRACT

The oxidation of glycolic, lactic, and malic and a few substituted mandelic acids by pyridinium dichromate (PDC) in dimethylsulphoxide (DMSO) lead to the formation of corresponding oxoacids. The reaction is first order each in PDC. Michaelis-Menten type of kinetics is observed with respect to the hydroxy acids. Reaction is failed to induce the polymerisation of acrylonitrile. The oxidation of α -deuteriomandelic acid shows the presence of a primary kinetic isotope effect ($k_H/k_D = 5.79$ at 298 K). The reaction does not exhibit the solvent isotope effect. The reaction is catalysed by the hydrogen ions. The hydrogen ion dependence has the form: $k_{obs} = a + b [H^+]$. Oxidation of p-methyl mandelic acid has been studied in 19 different organic solvents. The solvent effect has been analysed by using Kamlet's and Swain's multiparametric equations. A mechanism involving a hydride ion transfer via a chromate ester is proposed.

Keywords: Correlation analysis, dichromate, hydroxy acids, kinetics, mechanism, oxidation.
