



Oxidation of Aliphatic Primary Alcohols by Pyridinium Dichromate: A Kinetic and Mechanistic Study

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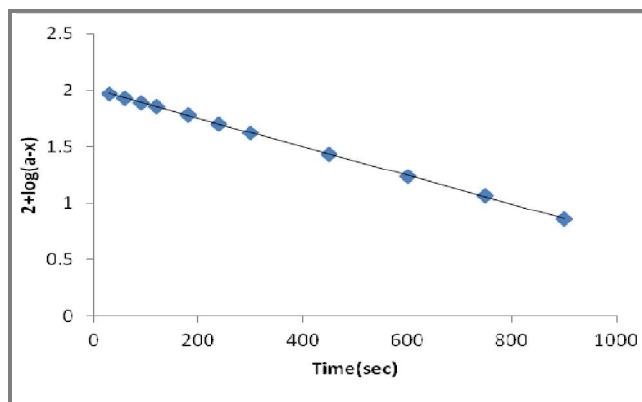
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ABSTRACT

The oxidation of nine aliphatic primary alcohols by pyridinium dichromate (PDC) in dimethylsulphoxide leads to the formation of corresponding aldehydes. The reaction is first order with respect to PDC. Michaelis-Menten type kinetics is observed with respect to alcohols. The reaction is promoted by hydrogen ions; the hydrogen ion dependence has the form $k_{obs} = a + b [H^+]$. The oxidation of [1, 1-²H₂] ethanol (MeCD₂OH) exhibits a substantial primary kinetic isotope effect ($k_H/k_D = 5.67$ at 298K). The reaction has been studied in nineteen different organic solvents. The solvent effect was analysed using Taft's and Swain's multiparametric equations. The rate of oxidation is susceptible to both polar and steric effects of the substituents. A suitable mechanism has been proposed.

Graphical Abstract



Oxidation of Ethyl alcohol by PDC: A typical Kinetic Run.

Keywords: Alcohols, dichromate, pyridinium, kinetics, mechanism, oxidation.