



Oxidation of Some Aliphatic Aldehydes by Pyridinium Dichromate: A Kinetic and Mechanistic Study

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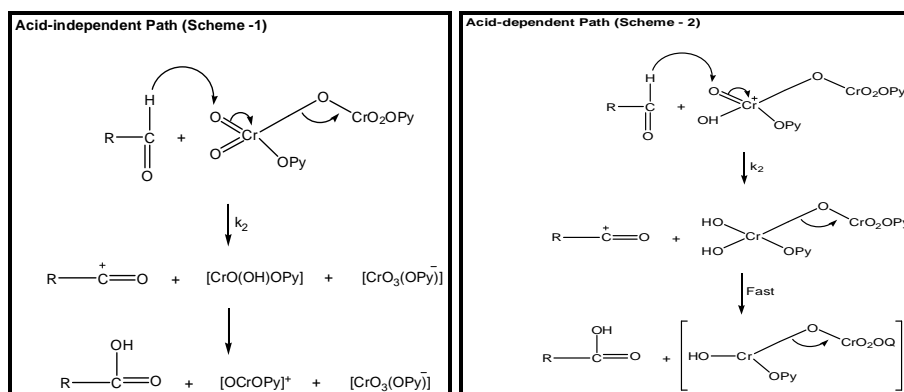
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ABSTRACT

The Oxidation of six aliphatic aldehydes by pyridinium dichromate (PDC) in dimethyl sulfoxide (DMSO) leads to the formation of corresponding carboxylic acids. The reaction is first order each in PDC. A Michaelis-Menten type of kinetics is observed with respect to the aldehydes. The reaction is catalyzed by hydrogen ions, the hydrogen-ion dependence has the form: $k_{obs} = a + b[H^+]$. The oxidation of deuteriated acetaldehyde, MeCDO, exhibited a substantial primary kinetic isotope effect ($k_H/k_D = 5.74$ at 298 K). The oxidation of acetaldehyde has been studied in nineteen different organic solvents. The solvent effect has been analyzed using Taft's and Swain's multiparametric equations. The rate constants correlate well with Taft's σ^* values; reaction constants being negative. A mechanism involving transfer of hydride ion has been suggested

Graphical Abstract



Keywords: Aldehydes, Correlation analysis, Halochromate, Kinetics, Mechanism, Oxidation.