



Kinetics and Mechanism of the Oxidation of some Vicinal and Non-vicinal Diols by Quinolinium Dichromate

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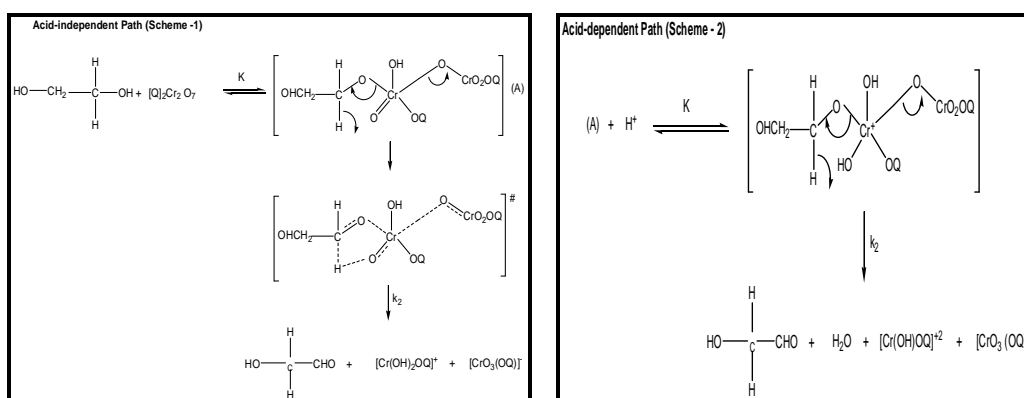
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ABSTRACT

The kinetics of oxidation of four vicinal, four non-vicinal diols by quinolinium dichromate (QDC) have been studied in dimethylsulphoxide (DMSO). The main product of oxidation is the corresponding hydroxycarbonyl compound. The reaction is first order in QDC. Michaelis-Menten type of kinetics is observed with respect to the diols. The reaction is catalysed by hydrogen ions. The hydrogen ion dependence has the form: $k_{obs} = a + b[H^+]$. The oxidation of [1,1,2,2-²H₄] ethanediol exhibits a substantial primary kinetic isotope effect ($k_H/k_D = 5.57$ at 298 K). The reaction has been studied in nineteen different organic solvents and the solvent effect has been analysed using Taft's and Swain's multiparametric equations. The temperature dependence of the kinetic isotope effect indicates the presence of a symmetrical transition state in the rate-determining step. A suitable mechanism has been proposed.

Graphical Abstract



Scheme

Keywords: Correlation analysis, dichromate, diols, kinetics, mechanism, oxidation.