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Kinetic and Mechanistic Studies in the Oxidative Regeneration of Carbonyl Compounds from Oximes by Quinolinium Chlorochromate

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ABSTRACT

The oxidative deoxidization of several aldol- and keto-oximes by quinolinium chlorochromate (QCC), in dimethylsulphoxide (DMSO), exhibited a first order dependence on QCC. Michaelis-Menten type kinetics was observed with respect to oximes. The oxidation of ketoximes is slower than that of aldoximes. The rates of oxidation of aldoximes correlated well in terms of Pavelich-Taft dual substituent-parameter equation. The low positive value of polar reaction constant indicated a nucleophilic attack by a chromate-oxygen on the carbon. The reaction is subject to steric hindrance by the alkyl groups. The reaction of acetaldoxime has been studied in nineteen different organic solvents. The solvent effect has been analysed by multiparametric equations. A mechanism involving the formation of a cyclic intermediate, in the rate-determining step is suggested.

Keywords: Carbonyl compounds, Dichromates, Kinetics, Mechanism, Oxidation, Oximes.