ISSN: 2278-1862



Journal of Applicable Chemistry

2018, 7 (6): 1771-1779 (International Peer Reviewed Journal)



Mechanism of the Oxidation of some α-Hydroxy acids by Imidazolium Dichromate

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Accepted on 7th November, 2018

ABSTRACT

The oxidation of glycolic, lactic, malic and a few substituted mandelic acids by imidazolium dichromate (IDC) in dimethylsulphoxide (DMSO) leads to the formation of corresponding oxoacids. The reaction is first order each in IDC. Michaelis-Menten type of kinetics is observed with respect to the hydroxy acids. Reaction is failed to induce the polymerization of acrylonitrile. The oxidation of α -deuteriomandelic acid shows the presence of a primary kinetic isotope effect ($k_H/k_D = 5.77$ at 298 K). The reaction does not exhibit the solvent isotope effect. The reaction is catalyzed 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 analyzed by using Kamlet's and Swain's multiparametric equations. A mechanism involving a hydride ion transfer via a chromate ester is proposed.

Graphical Abstract

Acid-independent Path (Scheme -1)

$$\begin{array}{c} \text{COOH} \\ \text{Ar} \quad \begin{array}{c} \text{COOH} \\ \text{OH} \end{array} \\ \text{H} \end{array} \begin{array}{c} \text{K} \\ \text{IIM}_2\text{Cr}_2\text{O}_7 \end{array} \begin{array}{c} \text{K} \\ \text{Ar} \quad \begin{array}{c} \text{COOH} \\ \text{OH} \end{array} \\ \text{OIM} \end{array} \begin{array}{c} \text{Ar} \quad \begin{array}{c} \text{COOH} \\ \text{OIM} \end{array} \end{array} \begin{array}{c} \text{Ar} \\ \text{OIM} \end{array} \begin{array}{c} \text{CrO}_2\text{OIM} \\ \text{Ar} \quad \begin{array}{c} \text{COOH} \\ \text{OIM} \end{array} \end{array} \begin{array}{c} \text{Ar} \\ \text{OIM} \end{array} \begin{array}{c} \text{CrO}_2\text{OIM} \end{array} \begin{array}{c} \text{CrO}_2\text{OIM} \\ \text{OIM} \end{array} \begin{array}{c} \text{COOH} \\ \text{OIM} \end{array} \begin{array}{c} \text{CrO}_2\text{OIM} \end{array} \begin{array}{c} \text{CrO}_2\text{OIM}$$

Scheme

Keywords: Correlation analysis, Dichromate, Hydroxy acids, Kinetics, Mechanism, Oxidation.