

Journal of Applicable Chemistry

2025, 14 (2): 207-216 (International Peer Reviewed Journal)



ISSN: 2278-1862

Structure-Reactivity Correlation in the Oxidation of Aliphatic Primary Alcohols by Tripropylammonium chlorochromate

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Accepted on 4th March, 2025

ABSTRACT

The oxidation of nine aliphatic primary alcohols by Tripropylammonium chlorochromate (TPACC) in dimethylsulfoxide leads to the formation of corresponding aldehydes. The reaction is first order with respect to TPACC. A 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 $[1,1^{-2}H_2]$ ethanol (MeCD₂OH) exhibits a substantial primary kinetic isotope effect ($k_H/k_D = 5.60$ 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:

Acid Independent Path

Keywords: Correlation analysis, Halochromates, Kinetics, Mechanism, Oxidation.

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