



Oxidation of Lower Oxyacids of Phosphorus by Imidazolium Dichromate: A Kinetic and Mechanistic Approach

Sonali Saraf, Kanchan Kanwar, S. Poonia, S. Panwar and Vinita Sharma *

*Chemical Kinetics Laboratory, Department of Chemistry, J.N.V. University, Jodhpur, Rajasthan, **INDIA**

Email: drpkvs27@yahoo.com

Accepted on 10th July 2017, Published online on 27th July 2017

ABSTRACT

Oxidation of lower oxyacids of phosphorus by imidazolium dichromate (IDC) in dimethylsulphoxide (DMSO) leads to the formation of corresponding oxyacids with phosphorus in a higher oxidation state. The reaction exhibits 1:1 stoichiometry. The reaction is first order with respect to IDC. A Michaelis-Menten type of kinetics was observed with respect to the reductants. The reaction does not induce polymerization of acrylonitrile. Reactions are catalyzed by hydrogen ions. The hydrogen-ion dependence has the form: $k_{obs} = a + b[H^+]$. The oxidation of deuteriated phosphinic and phenylphosphinic acids exhibited a substantial primary kinetic isotope effect. The oxidation was studied in nineteen different organic solvents. The solvent effects were analysed in terms of Taft's and Swain's multiparametric equations. The effect of solvent indicates the solvent polarity plays a major role in the process. It has been shown that the penta-coordinated tautomer of the phosphorus oxyacid is the reactive reductant and it has been concluded that tri-coordinated forms of phosphorus oxyacids does not participate in the oxidation process. A mechanism involving transfer of a hydride ion in the rate-determining step has been proposed.

Keywords: Dichromate, Kinetics, Mechanism, Oxidation, Phosphorus oxyacids.
