



Kinetics and Mechanism of the Oxidation of Formic and Oxalic acids by Quinolinium Dichromate

Rajesh Kumar, Shobha Puniya, Sonali Saraf,
Usha Songara and Vinita Sharma*

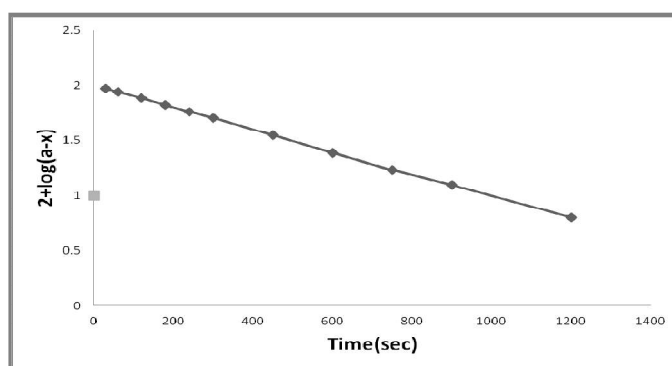
Chemical kinetics Laboratories, Department of Chemistry, J.N.V. University, Jodhpur, **INDIA**
E-mail: drpkvs27@yahoo.com

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ABSTRACT

Kinetics and mechanism of oxidation of formic and oxalic acids by quinolinium dichromate (QDC) have been studied in dimethylsulphoxide. The main product of oxidation is carbon dioxide. The reaction is first order with respect to QDC. Michaelis-Menten type of kinetics was observed with respect to the reductants. The reaction is acid catalysed and the acid dependence has the form: $k_{obs} = a + b [H^+]$. The oxidation of α -deuterio formic acid exhibits a substantial primary kinetic isotope effect ($k_H/k_D = 5.75$ 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 cyclic transition state in the rate determining step. Suitable mechanisms have been proposed.

Graphical Abstract



Oxidation of FA acid by QDC: A typical kinetic run.

Keywords: Acids, Dichromate, Kinetics, Mechanism, Oxidation.