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Kinetics and Mechanism of Ir(III)-Catalyzed Oxidation of D-Galactose by Potassium Iodate in Aqueous Alkaline Medium

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ABSTRACT

The kinetics of Ir (III)-catalyzed oxidation of galactose by potassium iodate in alkaline medium have been made at 40^0C.The reaction exhibits first-order kinetics with respect to Ir (III).Unity order at low concentrations of galactose, OH^- andIO_3^-becomes zero order at their higher concentrations throughout their variations. Negligible effects of Cl^- and ionic strength of the medium on the rate of oxidation have been noted. The reaction was studied at four different temperatures and observed values of rate constants were utilized to calculate various activation parameters. A most probable reaction mechanism consistent with the observed kinetic data and spectral evidence has been proposed for the oxidation of galactose.

Highlights:

1. The reactive species of KIO_3 is considered as $[IO_3^-]$.
2. $[IrCl_3(H_2O)_2OH^-]$ is considered to be the active species of Ir(III) chloride among the various species of Ir(III) chloride in alkaline medium.
3. The formation of a reactive complex, C_3, between reactive species of Ir(III) chloride and IO_3^- in alkaline medium is well supported by observed kinetic and spectral data.
4. Oxidation of D-galactose by iodate in alkaline medium is very sluggish, but it becomes facile in the presence of Ir(III) catalyst so It can be concluded that Ir(III) acts as an efficient catalyst in the oxidation of D-galactose by iodate in alkaline medium.
5. In step (III) of reaction scheme 1, an interaction between a charged species, C_3 and a neutral molecule, enediol resulting in the formation of most reactive activated complex is well supported by the observed positive entropy of activation and spectroscopic data.
6. Interaction between a charged species and a molecule confirms nil effect of ionic strength.
7. The positive value of $\Delta S^{\#}$ suggests that the intermediate complex is less ordered than the reactants. A high positive value of $\Delta G^{\#}$ indicates that the transition state is highly solvate.

Keywords: Mechanism, D-Galactose, Potassium iodate, Alkaline medium, Ir(III) Catalysis.