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The Kinetics of Rh(III)-Catalyzed Oxidation of D(+) Melibiose By Cu(II) Bipyridyl Complex In Alkaline Medium

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ABSTRACT

The kinetics of Rh(III)-catalyzed reaction between D(+)melibiose and $(Cu(Bip)_2^{2+})$ the reaction has been studied in the temperature range 35-50°C in alkaline medium. Kinetic data show that the rate of oxidation is independent of [Cu (II)] and follows first-order kinetics with respect to [Rh(III)]. Reaction shows fractional-positive order kinetics with respect to [OH⁻] and [D(+)melibiose]. In the present kinetic study, bipyridyl (Bip) was used as complexing agent so that the reaction mixture remains homogeneous throughout the course of reaction. Variations of [Bip] and ionic strength of the medium show nil effect on the rate of oxidation. The pseudo-zeroth-order rate constant decreases with increase in the dielectric constant of the medium. Various activation parameters including energy of activation along with entropy of activation were also calculated. Sodium salts of arabinonic acid, lyxonic acid and formic acid were identified as oxidation products of reaction under investigation. On the basis of the experimental findings, spectrophotometric observations, stoichiometric evidence and product analysis, a suitable mechanism has been proposed.

Graphical Abstract: The kinetics of Rh(III)-catalyzed reaction between D(+)melibiose and Copper(II) complexed with bipyridyl has been studied spectrophotometrically, for the first time, at 40°C in alkaline medium. The rate determining step of the reaction involves the formation of most reactive activated complex, which disproportionate into the products via fast steps.

$$\begin{bmatrix} H - C - O - RhCl_3(OH)(H_2O) \\ \parallel \\ C - OH \\ \parallel \\ R \end{bmatrix}$$

Keywords: Spectrophotometric study, D(+)melibiose, chlorocomplex of Rh(III), copper-bipyridyl complex, alkaline medium.