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Kinetic Studies of Rh (III)-Catalysed Oxidation of Mannose by N-Bromoacetamide in Alkaline Medium

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ABSTRACT

The kinetics of oxidation of mannose by N-bromoacetamide (NBA) in alkaline medium using Rh (III) as homogeneous catalyst have been studied at 40° C. The reaction exhibits first order kinetics with respect to [NBA], [Mannose] and [Rh (III)]. The rate of reaction is fractional positive order with respect to [OH]. The reaction remains unaffected by the change in ionic strength, [CI] and dielectric constant of the medium.There are no effects of [NHA] and [Hg(OAc)₂] on rate of reaction. Various activation parameters such as E_a , $\Delta S^{\#}$, $\Delta H^{\#}$, $\Delta G^{\#}$ and Arrhenius frequency factor (A) have been calculated for the reaction under investigation. The species [RhCl₃ (H₂O)₂(OH)]⁻ and [CH₃CONBr⁻] have been considered as the reactive species of Rh(III) chloride and NBA in alkaline medium respectively. On the basis of observed kinetic data, spectral information and activation parameters; a suitable mechanism for the oxidation of mannose has been proposed.

Graphical Abstract

Kinetics of oxidation of mannose by N-bromoacetamide (NBA) in alkaline medium using Rh(III) as homogeneous catalyst have been studied at 40° C. In the present study, the species [RhCl₃(H₂O)₂(OH)]⁻ and [CH₃CONBr⁻] have been considered as the reactive species of Rh(III) chloride and NBA in alkaline medium for the oxidation of mannose and also it was observed that the positive entropy of activation which clearly supports the interaction between the species, [RhCl₃(H₂O)(CH₃CONBr)OH]²⁻ and neutral

form of sugar
$$R^{-C-OH}$$
, leading to the formation of most reactive activated complex(C₄),
 $\begin{bmatrix} H \\ H-C-OH \\ R-C=O \rightarrow [RhCl_3 (CH_3CONBr) OH] \end{bmatrix}^2$, in the proposed reaction mechanism.

Keywords: Kinetics, N-bromoacetamide, Mannose, Rhodium, Alkaline medium.