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Journal of Applicable Chemistry

2015, 4 (2): 587-600 (International Peer Reviewed Journal)



ISSN: 2278-1862

A Kinetic Approach for $(H_2OBr)^+$ Oxidation of Glucose in Presence of $[RhCl_4(H_2O)_2]^{1-}$ as Catalyst

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Accepted on 2nd February 2015

ABSTRACT

The kinetics and mechanism of Rh (III)-catalyzed oxidation of D-glucose by N-bromoacetamide (NBA) in acidic medium has been studied at 40° C using Hg (OAc)₂ as scavenger for B⁻ ions. The reaction follows first-order kinetics in [NBA] at its lower concentration range tending towards zero order at its higher concentrations. The order of reaction was found to be unity with respect to Rh (III) throughout its variation. The reaction exhibits zero-order kinetics with respect to glucose and fractional positive order with respect to H⁺ and Cl⁻ in the oxidation of glucose. Negative effects of Hg (II) and NHA on the rate of reaction have been observed. The reaction remains unaffected by the change in ionic strength of the medium. Formic acid and arabinonic acid were identified as the main oxidation products of the 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. On the basis of observed kinetic data, spectral information and activation parameters, a suitable mechanism for the oxidation of D-glucose has been proposed. The most reactive activated complex, [RhCl₃(H₂O)₂(H₂OBr)] formed between reactive species of Rh(III) chloride and reactive species of NBA and an unreactive complex, [RhCl₄(H₂O)(H₂OBrHg)]²⁺, formed between Hg(II) and [RhCl₄(H₂O)(H₂OBr)], were identified by spectral evidence which supports the most probable reaction path proposed for the oxidation of D-glucose.

Keywords: D-Glucose, Oxidation, N-bromoacetamide, Rh (III) catalysis, Acidic medium, Kinetic study.