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Kinetics and mechanistic investigation of persulfate anion-mediated oxidation of hexacyanoruthenate(II) in aqueous medium

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The proposed study aimed to explore the kinetics of $[Ru(CN)_6]^{4-}$ oxidation in an aqueous media by persulfate anion ($S_2O_8^{2-}$). The increment in absorbance at 460 nm, which is indicative of the concentration of $[Ru(CN)_6]^{3-}$, was measured to determine the reaction rate. Applying the pseudo-first-order state, the reaction's progression was analyzed as an indicator of $[Ru(CN)_6^{4-}]$, temperature, $[S_2O_8^{2-}]$, ionic strength, and *p*H. The findings indicate that the *p*H of the medium is the crucial factor that significantly affects the rate of the reaction. The $[Ru(CN)_6]^{4-}$ undergoes a 2:1 stoichiometric interaction with $S_2O_8^{2-}$. The observed reaction exhibits first-order kinetics with regard to $[Ru(CN)_6^{4-}]$, and $[S_2O_8^{2-}]$, within the range of concentrations investigated. The observed invariance in reaction rate upon electrolyte's introduction is suggestive of a zero salt effect. The electron transfer from $[Ru(CN)_6]^{4-}$ to $S_2O_8^{2-}$ proceeds *via* the formation of ion-pair, which leads to the formation of $[Ru(CN)_6]^{3}$, sulfate ion, and sulfate radical ion. The formation of ion-pair is strengthened by the zero salt effect, while, the comparatively low activation energy and free radical test supports the formation of sulfate radical ion during the course of the reaction. The outer-sphere electron transfer pathway, *via* the formation of ion-pair as proposed by us, is further supported by the negative entropy of activation value.

Keywords: Persulfate, Oxidation, Hexacyanoruthenate(II), Kinetics and Mechanism, Ion-pair, Salt effect