

Kinetics and Mechanism of Oxidation of Oxalic Acid with Bi(V) in HClO₄-HF Mixture



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ABSTRACT

The kinetics of oxidation of oxalic acid with Bi(V) has been investigated in HClO₄ (1.0M) and HF (1.5M) mixture. The rate followed first order kinetics each in Bi(V) and oxalic acid. The reaction rate is independent of [H⁺]. Addition of HF and (F⁺) has not effect on the reaction rate. The reaction rates decreased with the increase in ionic strength. The mode of electron transfer from the substrate to Bi (V) has been indicated via bridged outer sphere mechanism.

The kinetics investigation were carried out at 20,25 and 30°C and calculated second order rate constant (k) are found to be $(6.2 \pm 2) \times 10^{-2}$, $(8.6 \pm 0.31) \times 10^{-2}$ and $(10.3 \pm 0.12) \times 10^{-2} \text{ mol}^{-2} \text{ dm}^3 \text{ s}^{-1}$ respectively. The thermodynamic parameters were calculated in a conventional method. The energy of activation (E_a) and entropy of activation (ΔS^{*}) are found to be $(45.19 \pm 0.34) \text{ KJ mol}^{-1}$ and $(-113.92 \pm 2) \text{ J K}^{-1}$, respectively at 20°C . The low value of energy of activation but high negative value of entropy of activation may be ascribed to the hydrogen bonded intermeidate, which causes a facile electron transference from oxygen atom to Bi(V).

Keywords: Kinetics, Oxidation, Oxalic acid, Bi(V),HClO₄-HF Mixture.