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Kinetics and mechanism of osmium (VIII) catalysed oxidation of formic acid by hexacyanoferrate (III) in aqueous alkaline medium

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The kinetics of osmium (VIII) catalysed oxidation of formic acid by hexacyanoferrate (III) in alkaline medium is investigated.

There are two main basic reasons for employing $[Fe(CN)_6]^{3-}$ as an efficient reagent for oxidation of variety of organic substrates. Firstly, the oxidation potential of $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ redox couple over a wide pH range remains constant making it a reagent of selective oxidations.

Secondly the oxidized and reduced forms are appreciably stable and substitutionally inert. Since the ligands CN^- are resistant to substitution, outer-sphere electron transfer is the preferred mode of oxidation reactions[12].

The kinetics of osmium (VIII) catalysed oxidation of formic acid by hexacyanoferrate (III) in alkaline medium has been studied. The stoichiometry of the reaction corresponds to the reaction as represented by the eqn (1)

$$HCO_2^- + 2[Fe(CN)_6]^{3-} + OH^- \rightarrow 2[Fe(CN)_6]^{4-} + CO_2 + H_2O \quad (1)$$

The kinetics of the reaction were monitored by estimating hexacyanoferrate (III) at 420 nm employing spectronic 21 without any interference from osmium (VIII) and its reduction product. However, hexacyanoferrate (II) is transparent at this wavelength[16]. The kinetic measurements in triplicate were reproducible to within ± 5%.

The kinetic orders with respect to the catalyst and the substrate are one each, however, the rate is independent of the oxidant concentration. Hydroxide ion dependence is complex. The osmium (VIII) species in alkaline solution are governed[20,21] by the equilibrium (3).

$$[OsO_3(OH)_3]^- + OH^- \overset{K}{\rightleftharpoons} [OsO_4(OH)_2]^{2-} + H_2O \quad (3)$$

The equilibrium constant K for this step (3) has been determined to be 22 ± 4, 32 ± 6 and 42 ± 6 $dm^3\,mol^{-1}$ at 25, 35 and 45 °C respectively and $I = 1.0$ $moldm^{-3}$.

The species $[OsO_4\,(OH)_2]^{2-}$ has been considered to be the reactive form of the catalyst. The mechanism of the reaction has been proposed as follows.

$$[OsO_3(OH)_3]^- + OH^- \overset{K}{\rightleftharpoons} [OsO_4(OH)_2]^{2-} + H_2O \quad (3)$$

$$[OsO_4(OH_2]^{2-} + HCO_2^- \overset{K}{\rightleftharpoons} [OsO_4(OH)_2.HCO_2]^{3-} \quad (4)$$

$$[OsO_4(OH)_2.HCO_2]^{3-} + H_2O \xrightarrow{k} [OsO_2(OH)_4]^{2-} + OH^- + CO_2 \quad (5)$$

$$[OsO_2(OH)_4]^{2-} + 2[Fe(CN)_6]^{3-} \xrightarrow{\text{Fast}} [OsO_2(OH)_4] + 2[Fe(CN)_6{}^{4-}] \quad (6)$$

$$[OsO_2(OH)_4] + 2OH^- \xrightarrow{\text{Fast}} [OsO_4(OH)_2]^{2-} + 2H_2O \quad (7)$$

Such a mechanism leads to the rate law (8)

$$\frac{-\,d[Fe(CN)_6]^{3-}}{dt} = \frac{2kK'K[Os(VIII)]\,[OH^-]\,[HCO_2^-]}{1 + K\,[OH^-]} \quad (8)$$

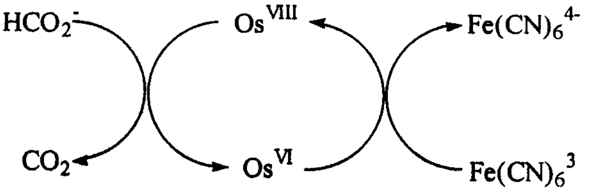
However at constant concentration of hydroxide ion, the rate law (8) changes to eqn (9)

$$\frac{-\,d[Fe(CN)_6]^{3-}}{dt} = k_2[Os(VIII)][HCO_2^-] \quad (9)$$

where $k_2 = 2kK'$

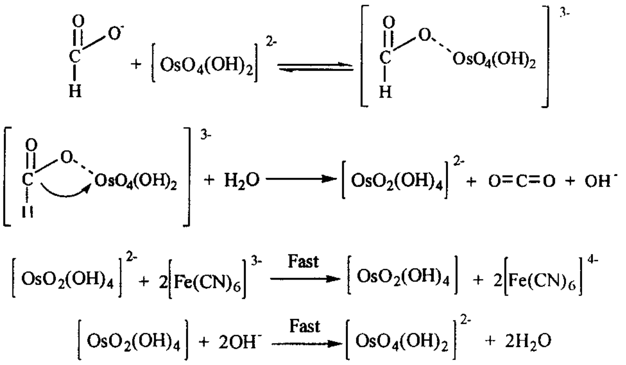
A plot of $(k_2)^{-1}$ versus $[OH^-]$ from the eqn (8) yields a straight line with non-zero intercept, K was calculated from the ratio of the intercept and gredient in agreement with the value calculated spectrophotometrically and also the value reported[18] elsewhere.

The role of the catalyst has been assigned to the operation of the catalyst redox cycle as in Scheme 1



Scheme 1

However, the preferential mode of the electron transfer has been considered through hydride ion transfer as in Scheme 2



Scheme 2

The effect of electrolytes on the rate has been assigned to specific cation effect in the absence of the rate dependence on the concentration of hexacyanoferrate (III). A comparative analysis of the oxidation of formic acid with other metal ion oxidants have also been made.

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[†] This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*