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NOTE

A Kinetic Study of Iridium(III) Chloride Catalyzed Oxidation of Diethylene Glycol by Hexacyanoferrate(III) in Aqueous Alkaline Medium

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The iridium(III) chloride catalyzed oxidation of diethylene glycol by hexacyanoferrate(III) in aqueous alkaline medium has been studied at constant ionic strength and temperature. The reaction follows first order kinetics with respect to hydroxide ion and organic substrate at lower concentration but at higher concentrations it follows zero order kinetics. The order of reaction with respect to hexacyanoferrate(III) and iridium trichloride is unity even up to manyfold variation. A probable reaction mechanism is proposed assuming that the reaction proceeds through complex formation.

Key Words: Kinetics, Iridium(III) chloride, Oxidation, Diethylene glycol, Hexacyanoferrate(III).

There are so many homogeneously catalyzed oxidation reactions in solution which have been subjected to detailed kinetic study. Oxidation of organic compounds by hexacyanoferrate(III) (abbreviated as HCF) in alkaline medium is one of them. In these reactions many platinum metals as ruthenium, rhodium and osmium[1–5] etc. have been used as catalyst. But the use of iridium trichloride in the above said oxidation reactions is very less[6, 7]. Thus in the present study an attempt has been made to study the oxidation of diethylene glycol by HCF in aqueous alkaline medium.

All chemicals and reagents used were of analytical grade and all solutions were prepared in doubly distilled water. The solution of iridium trichloride was prepared by dissolving the sample in a very dilute solution of HCl. The ionic strength of the system was kept constant by using KCl. The temperature of the reaction was maintained within the accuracy of ±0.1°C. The progress of the reaction was measured at different intervals of time by estimating the amount of HCF produced with a standard solution of ceric(IV) sulphate using ferroin as indicator.

The results reveal that the oxidation of diethylene glycol follows first order kinetics at lower concentration of hydroxide ion which tends to become independent at its higher concentration. The concentrations of OH^- and organic substrate were varied from 0.1 to 1.0 M and 0.01 to 0.1 M respectively. The straight line plot confirms the first order kinetics with respect to HCF which is varied from 0.001 to 0.01 M. The effect of variation of iridium trichloride shows first order kinetics up to its manyfold variation. A plot of log rate *vs.* $\sqrt{\mu}$ has been found to be a straight line showing positive salt effect.

Mechanism

The mechanism has been proposed by the following reactions:

$$GS + OH^- \overset{K}{\rightleftharpoons} GS^- + H_2O \tag{i}$$

$$GS^- + Ir^{3+} \overset{K_1}{\rightleftharpoons} C_1 \tag{ii}$$

$$C_1 + [Fe(CN)_6]^{3-} \overset{K_2}{\rightleftharpoons} C_2 \tag{iii}$$

$$C_2 \xrightarrow[\text{(slow)}]{k} Ir^+ + Fe(CN)_6]^{4-} + \text{I.P.} \tag{iv}$$

$$Ir^+ + 2[Fe(CN)_6]^{3-} + H_2O \xrightarrow{\text{(fast)}} Ir^{3+} + 2[Fe(CN)_6]^{4-} \tag{v}$$

$$\text{I.P.} \xrightarrow[\text{(fast)}]{\text{(oxid)}} \text{Acid} \tag{vi}$$

where GS represents organic substrate which forms an anion[8] with hydroxide ion. The anion and Ir^{3+} form a loosely bonded complex C_1. The complex C_1 again combines with ferricyanide ion to give another complex C_2. The complex C_2 then slowly decomposes into Ir^{3+} and I.P. (intermediate product). The I.P. is further oxidised to final product acid.

After applying steady treatment to the above reaction mechanism, the following rate law has been derived

$$\text{rate} = -\frac{d[HCF]}{dt} = \frac{kKK_1K_2[S][OH^-][Ir^{3+}][HCF]_t}{1 + KK_1K_2[S][OH^-][Ir^{3+}]} \tag{1}$$

Rate law (1) clearly explains the nature shown by HCF, GS, OH^- and $IrCl^{3-}$ at low concencentrations. It can be explaind by assuming that $1 \gg KK_1K_2[S][OH^-][Ir^{3+}]$ at low concentrations and eq. (1) reduces to

$$-\frac{d[HCF]}{dt} = kKK_1K_2[S][OH^-][Ir^{3+}][HCF]_t \tag{2}$$

At higher concentration its inverse is true and eq. (2) becomes

$$-\frac{d[HCF]}{dt} = k[HCF]_t \tag{3}$$

Eq. (3) clearly explains first order kinetics w.r.t. HCF even up to its manyfold variations. The validity of rate law might be made by rewriting eq. (1) as

$$\frac{1}{\text{rate}} = [\text{kKK}_1\text{k}_2[\text{S}][\text{OH}^-][\text{Ir(III)}][\text{HCF}]_t]^{-1} + [\text{k}[\text{HCF}]]^{-1} \quad (4)$$

The plots of rate^{1-} *vs.* $[\text{S}]^{1-}$ and $[\text{OH}^-]^{1-}$ give straight line with positive intercept at y-axis. The k values calculated from the intercept are 1.67×10^{-2} and 0.68×10^{-2} min. There is close similarity in kKK_1K_2 values calculated from the slope of these curves, *i.e.*, 1.11×10^4 and 0.62×10^4 respectively. These straight line plots and positive intercepts and k values clearly confirm validity of rate law and proposed reaction mechanism.

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