Asian Journal of Chemistry Vol. 18, No. 2 (2006), 1116–1120

Iridium(III) Catalyzed Oxidation of Propane-1,2-diol by Hexacyanoferrate(III) in Aqueous Alkaline Medium: A Kinetic and Mechanistic Study

ANJALI GOEL*, MANISHA CHAUHAN and SHAILJA
Department of Chemistry
Gurukul Kanya Mahavidyalaya, Gurukul Kangri University
Jwalapur, Haridwar-249 407, India

Kinetics and mechanism of oxidation of propane-1,2-diol by hexacyanoferrate(III) in aqueous alkaline medium catalyzed by iridium(III) chloride has been studied at constant ionic strength (KCl) and temperature. The reaction follows first order kinetics with respect to hexacyanoferrate(III), $[OH^-]$ and organic substrate at lower concentrations, but at higher concentrations it follows zero order kinetics. The effect of variation of iridium(III) chloride shows first order kinetics even up to its manifold variation. A probable reaction mechanism is proposed assuming that the reaction proceeds through complex formation.

Key Words: Kinetics, Iridium(III) chloride, Oxidation, Propane-1,2-diol, Hexacyanoferrate(III).

INTRODUCTION

The present report is in continuation of our previous reports on iridium(III) catalyzed oxidation of alcohols by HCF(III) ions in aqueous medium[1, 2]. Here we report our results of the kinetic mechanistic studies on the iridium(III) chloride catalyzed oxidation of propane-1,2-diol (PDL-1,2) by alkaline solution of hexacyanoferrate(III) ion (HCF).

EXPERIMENTAL

Aqueous solution of PDL-1,2 (E. Merk) was prepared afresh. The solution of iridium(III) chloride (SRL) was prepared by dissolving the sample in a very dilute solution of hydrochloric acid. Sodium hydroxide and HCF(III) of CDH/AR grade was used. The ionic strength of the system was kept constant by using potassium chloride (E. Merck) solution. The experimental procedure is the same as discussed in our previous communication[3, 4].

Final products were confirmed by TLC and spot test method was reported earlier[5]. The final oxidation products were oxalic acid and acetic acid. The solvent used was the solution of *n*–butanol, formic acid and water. The value of 'r' (regression coefficient) is calculated by statistical methods[6].

RESULTS AND DISCUSSION

The iridium(III) chloride catalyzed oxidation of PDL-1,2 has been studied by alkaline HCF(III) in aqueous alkaline medium at 35°C. The results show (Fig. 1) first order dependence of reaction rate at lower concentrations of HCF(III) which tends to become independent at its higher concentrations. The concentration of HCF(III) has been varied from 1.0×10^{-3} to 0.9×10^{-3} M. The same type of trend is shown by the rate of reaction with respect to substrate and hydroxide ion (Figs. 2, 3). Propane-1,2-diol and hydroxyl ion concentration were varied from 1.0×10^{-2} to 10×10^{-2} M and 0.04 to 0.4 M respectively. The effect of variation of iridium(III) shows first order ($r^2 = 1.000$) kinetics even up to its manifold variation. The change in ionic strength of medium has a direct relationship with the rate of reaction indicating a positive salt effect, which has been shown in Fig. 4 ($r^2 = 0.9928$). The rate measurements were carried out at 30, 35, 40, 45 and 50°C and the energy of activation was calculated which was found to be 6.91 kcal/mol from the plot of log (–dc/dt) *vs.* 1/T ($r^2 = 0.9958$).

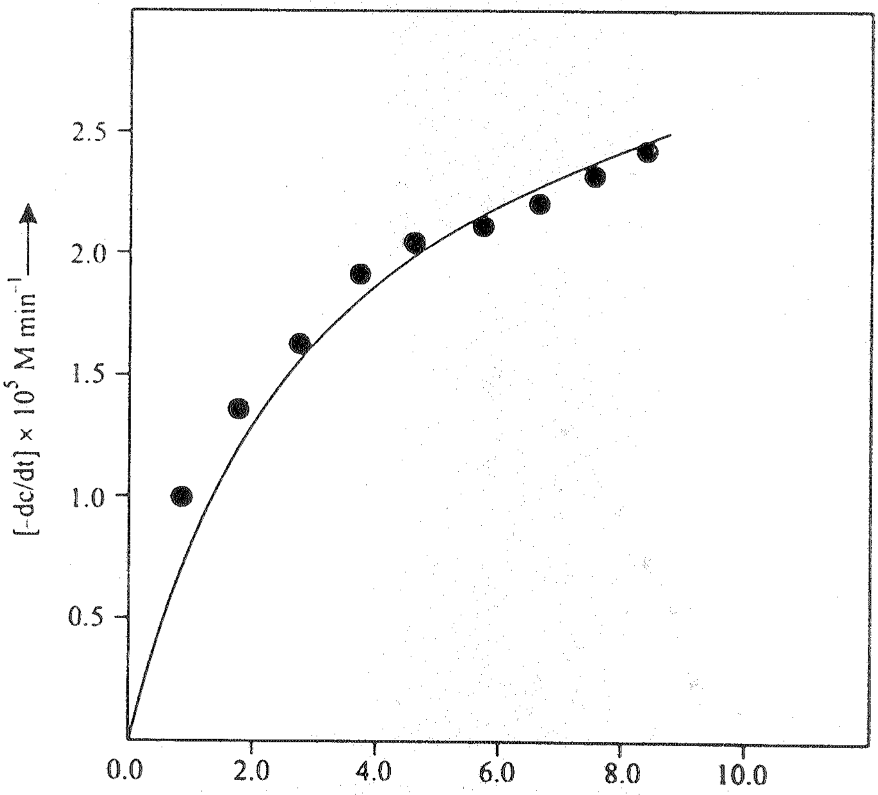

Fig. 1. Effect of [HCF(III)] on the rate of oxidation of PDL-1, 2 by alk. HCF(III) at 35°C. [PDL-1,2] = 6.00×10^{-2} M, [NaOH] = 0.40 M, [$IrCl_3$] = 5.36×10^{-5} M, $\mu = 0.50$ M

By studying the stoichiometry, it has been found that 8 mol of HCF(III) were consumed for the oxidation of 1 mol of each PDL-1,2.

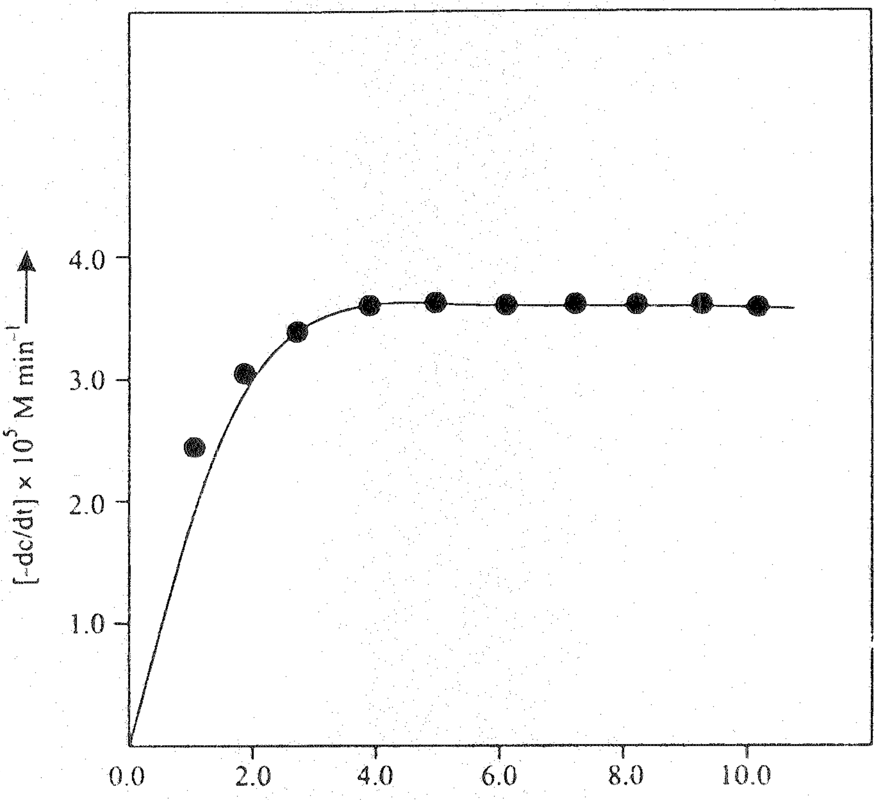

Fig. 2. Effect of [PDL-1,2] on the rate of oxidation by alk. HCF(III) ion at 35°C. [HCF(III)] = 2.00×10^{-3} M, [NaOH] = 0.20 M, [$IrCl_3$] = 5.36×10^{-5} M, $\mu = 0.50$ M

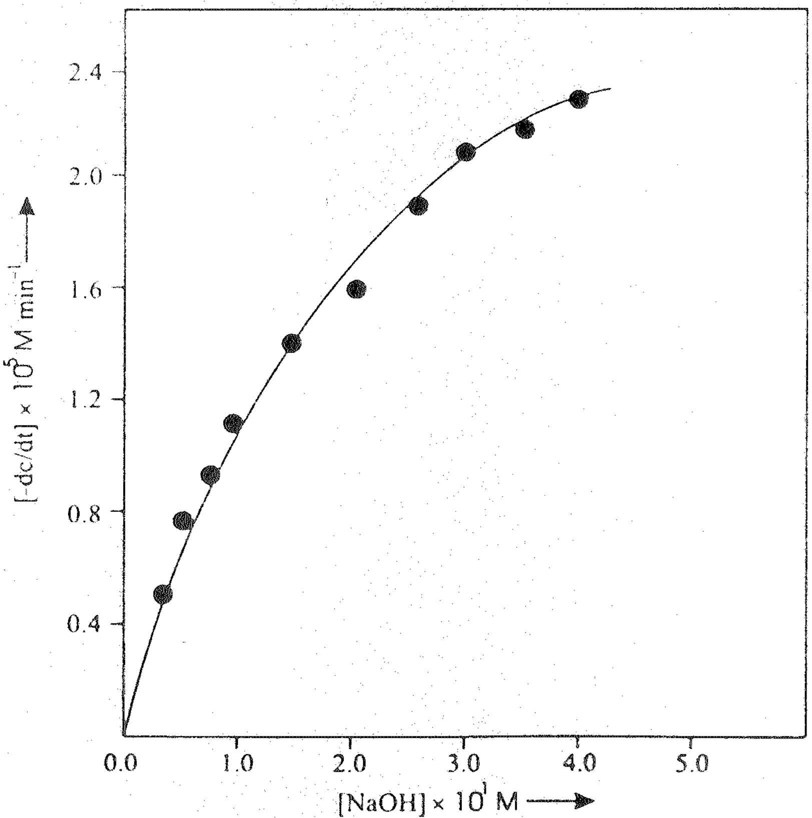

Fig. 3. Effect of [NaOH] on the rate of oxidation of PDL-1,2 by alk. HCF(III) ion at 35°C. [HCF(III)] = 3.00×10^{-3} M, [PDL-1,2] = 0.40×10^{-2} M, [$IrCl_3$] = 5.36×10^{-5} M, $\mu = 0.50$ M

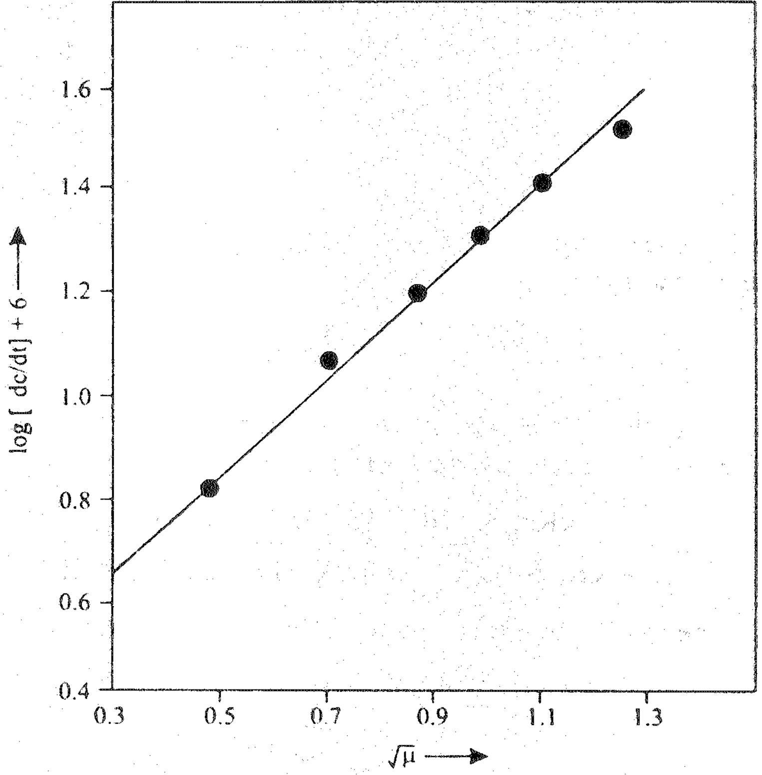

Fig. 4. Effect of [ionic strength] on the rate of oxidation of PDL-1,2 by alk. HCF(III) at 35°C. [HCF(III)] = 3.00 × 10^{-3} M, [NaOH] = 0.20 M, [PDL-1,2] = 4.00 × 10^{-3} M, [$IrCl_3$] = 5.36 × 10^{-5} M

Mechanism

The following rection mechanism is proposed for the oxidation of PDL-1,2 based on the results and product analysis.

$$RCH_2OH + OH^- \overset{K}{\rightleftharpoons} RCH_2O^- + H_2O$$

$$RCH_2O^- + IrCl_6^{3-} \overset{K_1}{\rightleftharpoons} \underset{C_1}{[RCH_2O\cdots\cdots IrCl_6]}$$

$$\underset{C_1}{[RCH_2O\cdots\cdots IrCl_6]} + Fe(CN)_6^{3-} \overset{K_2}{\rightleftharpoons} \underset{C_2}{[RCH_2O\cdots\cdots IrCl_6\cdots\cdots Fe^{3+}]}$$

$$[RCH_2O\cdots\cdots IrCl_6\cdots\cdots Fe^{3+}] \xrightarrow[\text{Slow}]{k} Cl^- + IrCl_5^{4-} + Fe^{2+} + \text{Intermediate Product}$$

$$IrCl_5^{4-} + 2Fe(CN)_6^{3-} + H_2O \xrightarrow{\text{Fast}} [IrCl_5 \cdot H_2O]^{2-} + 2Fe(CN)_4^{4-}$$

$$\text{Intermediate product} \xrightarrow{\text{Oxidation}} \text{Final product}$$

$$[IrCl_5 \cdot H_2O]^{2-} + Cl^- \xrightarrow{\text{Fast}} IrCl_6^{3-} + H_2O$$

$R = {}^-CH_2OH \cdot CH_3$.

It has been assumed that substrate reacts with hydroxide ions to form an anion (RCH_2O^-). This anion forms a loosely bonded complex (C_1) with iridium(III) which combines with HCF(III) to give another complex (C_2). The complex (C_2) then slwly disproportionates into Ir^{1+} and HCF(II) along with the intermediate product. The intermediate product is further oxidized to the final product. Ir^{1+} is reoxidized to Ir^{3+} by two molecules of HCF(III) *via* one electron transfer process. It is reported in our previous publication[4] that reacting species of iridium are Ir^{1+} and Ir^{3+}, not Ir^{2+}.

During the above proposed mechanism the disproprotionation of complex C_2 in intermediate complex is the slowest step. Thus according to the proposed mechanism, the rate of reaction 'r' is:

$$r = \frac{-d[HCF(III)]}{dt} = K[C_2] \qquad (1)$$

By calculating the concentration of C_2 in terms of $[Ir^{3+}]_t$, [S], $[OH^-]$ and [HCF(III)], the following rate law has been derived:

$$r = \frac{kKK_1K_2[HCF(III)][Ir^{3+}]_t[S][OH^-]}{1 + KK_1[S][OH^-] + KK_1K_2[S][OH^-][HCF(III)]} \qquad (2)$$

where $[Ir^{3+}]_t$ is the total concentration of iridium(III) in the form of Ir^{3+}, complexes C_1 and C_2.

Rate law (2) has been confirmed by rewriting the equation as below:

$$\frac{1}{r} = \frac{1}{kKK_1K_2[HCF(III)][Ir^{3+}]_t[S][OH^-]} + \frac{1}{kK_2[HCF(III)][Ir]_t} + \frac{1}{K[Ir^{3+}]_t} \qquad (3)$$

It is found that the graphs plotted between r^{-1} *vs.* $[S]^{-1}$ and r^{-1} *vs.* $[OH^-]^{1-}$ are straight line. The values of k and kKK_1K_2 were calculated with the help of the intercept and slopes of these plots betwen 1/r *vs.* 1/[S] and $1/[OH^-]$. The values are presented in Table-1.

TABLE-1

Name of substrate	Value of k		Value of kKK_1K_2	
	$\frac{1}{r}$ *vs.* $\frac{1}{[S]}$	$\frac{1}{r}$ *vs.* $\frac{1}{[OH^-]}$	$\frac{1}{r}$ *vs.* $\frac{1}{[S]}$	$\frac{1}{r}$ *vs.* $\frac{1}{[OH^-]}$
PDL-1,2	0.424	0.444	2.32×10^4	2.39×10^4

The constancy in values of 'k' and 'kKK_1K_2' clearly confirms the validity of rate law and the proposed mechanism.

REFERENCES

1. A. Goel and M. Chauhan, *Asian J. Chem.*, **16**, 1200 (2004).
2. A. Goel, G.R. Verma and H.S. Singh, *Himalayan J. Environ. Zool.*, **2**, 11 (1997).
3. S.K. Seth, A. Goel, G.R. Verma and H.S. Singh, *Asian J. Chem.*, **13**, 505 (2001).
4. A. Goel, G.R. Verma and H.S. Singh, *J. Indian Chem. Soc.*, **79**, 665 (2002).
5. F. Feigl, Spot Test in Organic Chemistry, Elsevier, New York, pp. 869–886 (1960).
6. S. Prasad, Elements of Biostatistics, 1st Edn., p. 180 (2003)

(*Received*: 28 April 2005; *Accepted*: 12 December 2005) AJC-4541