

Kinetics of Iridium(III) Catalysed Oxidation of Butane 1:4-Diol with Alkaline Hexacyanoferrate(III)

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Studies of the kinetics of iridium(III) chloride catalysed oxidation of butane-1:4-diol by aqueous alkaline hexacyanoferrate(III) (HCF) were made at constant ionic strength. The results suggest the complex formation between iridium(III) species and the substrate anion. This complex with hexacyanoferrate(III) gives another complex which slowly decomposes into univalent Ir(I) species and the intermediate products which in turn are further oxidised by HCF(III) into the subsequent steps.

INTRODUCTION

Recently a number of homogeneously catalysed oxidation reactions in solution have been subjected to detailed kinetic study. In the oxidation of organic compounds by hexacyanoferrate(III), in aqueous alkaline medium, platinum metals had been used as catalyst. Krishna *et al.*^{1,2} were the first to carry out osmium tetroxide catalysed oxidation of methanol and ethanol by hexacyanoferrate(III). Later on ruthenium(III) chloride has been used in the oxidation of amines³, glycols⁴ and benzyl amines⁵ etc. But literature on iridium(III) catalysed oxidation is scanty⁶. For further information concerning the oxidation kinetics of diols in alkaline medium, we report in this paper our results on the kinetics of oxidation of butane-1:4-diol by hexacyanoferrate(III).

EXPERIMENTAL

All chemicals and reagents used were of BDH, AR grade. Doubly distilled water was used to prepare the solution. The solution of iridium(III) chloride was prepared by dissolving the sample (Johnson Matthey and Co. Ltd.) in a solution of HCl. The temperature of the reaction was electrically thermostated within the accuracy of $\pm 0.1^\circ\text{C}$. The progress of the reaction was measured at different intervals of time by estimating the amount of hexacyanoferrate(III) produced with a standard solution of ceric(IV) sulphate using ferroin as indicator. The final oxidation product was confirmed by TLC studies.

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RESULTS AND DISCUSSION

Details of kinetic data for the rate of iridium(III) chloride catalysed oxidation of butane-1:4-diol are presented in Table-1. The results show first order dependence of reaction rate at lower concentrations of hexacyanoferrate(III) which becomes independent at its higher concentrations. The initial rates were calculated by plotting remaining hexacyanoferrate(III) vs. time. The variation of concentration of hydroxide ion, organic substrate and catalyst for many folds show first order dependence of reaction rates on concentration of organic substrate, hydroxide ion and organic substrate respectively. The change in ionic strength of medium (adjusted and maintained by addition of suitable amount of KCl) brings about significant change in $(-dc/dt)$ values showing positive salt effect. The rate measurements were carried out at 35, 40, 45, 50 and 55°C and the energy of activation was calculated which was found to be 14.560 kcal/mole from the plot of $\log(-dc/dt)$ vs. $(1/T)$.

TABLE-1
EFFECT OF VARIATION OF [REACTANTS] ON REACTION RATES AT 35°C

(A) Variation of hexacyanoferrate(III) concentration:

[Butane-1:4-diol] = 0.1 M; [NaOH] = 0.1 M; $\mu = 0.25$ M; $[\text{IrCl}_3] = 5.66 \times 10^{-5}$ M

$[\text{K}_3\text{Fe}(\text{CN})_6] \times 10^3$ M	0.60	1.12	2.14	3.14	4.00	4.88	6.00	7.00	8.00	8.64
$[-dc/dt] \times 10^7$ mL ⁻¹ min ⁻¹	2.8	3.3	4.5	5.9	6.6	6.8	8.0	8.8	9.2	9.6

(B) Variation of butane-1:4-diol concentration:

[HCF] = 2.0×10^{-3} M; [NaOH] = 0.08 M; $\mu = 0.25$ M; $[\text{IrCl}_3] = 5.66 \times 10^{-5}$ M

[Butane-1:4-diol] $\times 10^2$ M	6.00	8.00	10.00	12.00	14.00	16.00	18.00	20.00
$[-dc/dt] \times 10^7$ mL ⁻¹ min ⁻¹	1.8	3.2	4.6	6.2	8.2	9.8	11.4	13.0

(C) Variation of hydroxide ion concentration:

[HCF] = 2.5×10^{-3} M; [Butane-1:4-diol] = 0.1 M; $\mu = 0.25$ M; $[\text{IrCl}_3] = 5.66 \times 10^{-5}$ M

[NaOH] $\times 10^2$ M	1.00	2.00	3.00	4.00	5.00	6.00	7.00	8.00	9.00
$[-dc/dt] \times 10^7$ mL ⁻¹ min ⁻¹	1.11	2.33	3.21	4.00	5.33	7.10	8.50	9.70	12.50

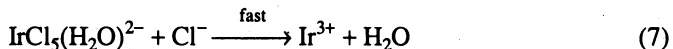
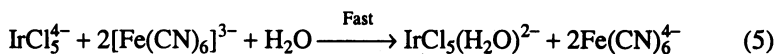
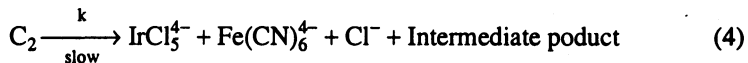
(D) Variation of iridium(III) chloride concentration:

[HCF] = 2.5×10^{-3} M; [Butane 1 : 4 diol] = 0.1 M; $\mu = 0.25$ M; NaOH = 0.1 M

$[\text{IrCl}_3] \times 10^5$ M	1.415	2.830	4.245	5.660	7.075	8.490
$[-dc/dt] \times 10^7$ mL ⁻¹ min ⁻¹	5.00	10.00	13.33	18.00	20.00	25.00

Mechanism: The results given in Table-1 clearly led us to propose the following reaction mechanism through electron transfer process which is made easier by metal ion⁷ complexing with the organic reducing group.





where 'S' stands for butane-1:4-diol and C_1 is a labile complex between Ir^{3+} and anion of organic substrate. C_2 represents complex between C_1 and hexacyanoferrate(III) ion. The exact nature of complex could not be discussed but it is assumed that the organic substrate and Ir^{3+} form a loosely bonded complex C_1 which combines with hexacyanoferrate(III) to give another complex C_2 ^{8,9}. This complex C_2 slowly decomposes into Ir^{3+} and $Fe(CN)_6^{4-}$ along with intermediate product. The intermediate product is further oxidized to final product. The rate of reaction 'r' is measured in terms of rate of disappearance of hexacyanoferrate(III).

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

At very low concentration of hydroxide organic substrate and hexacyanoferrate(III), equation (2) reduces to

$$r = 2kKK_1K_2[HCF][Ir^{3+}]_T[S][OH^-] \quad (ii)$$

This equation is inconsistent with the observed kinetics. At higher concentrations the validity of rate law might be ensured by rewriting equation (i) as follows

$$\frac{1}{r} = \frac{1}{2kKK_1K_2[HCF][Ir^{3+}]_T[S][OH^-]} + \frac{1}{2kK_2[HCF][Ir^{3+}]_T} + \frac{1}{2k[Ir^{3+}]_T} \quad (iii)$$

The values of k and kKK_1K_2 were calculated with the help of the intercept and slopes of plots between $1/R$ vs. $1/[s]$ and $1/R$ vs. $1/[OH^-]$. The values are presented in Table-2.

TABLE-2

Rate constant	(1/r)vs (1/[s])	(1/r)vs (1/[OH ⁻])	(1/r)vs (1/[Ir ³⁺])
kKK_1K_2	3.04×10^2	4.06×10^2	8.60×10^2
k	4.90×10^{-2}	4.41×10^{-2}	5.00×10^{-2}

The constancy in values of k and kKK_1K_2 clearly confirms the validity of rate law and the proposed mechanism. The final oxidation product succinic acid was confirmed by TLC method.

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