



## A KINETIC STUDY OF IRIDIUM (III) CHLORIDE CATALYZED OXIDATION OF SOME DIOLS BY ALKALINE HEXACYANOFERRATE (III) IN AQUEOUS MEDIUM

G. R. VERMA<sup>a</sup>, S. K. SETH<sup>b</sup>, ANJALI GOEL<sup>b\*</sup> and SHAKUNJ<sup>b</sup>

<sup>a</sup>Chemistry Department, S.D. (PG) College, MUZAFFARNAGAR-251001 (U.P.) INDIA

<sup>b\*</sup>Department of Chemistry, Kanya Gurukula Mahavidhyalaya  
Gurukul Kangri Vishwavidhyalaya, HARDWAR - 249407, (U.A.) INDIA  
Email : dr-anjaligoel@rediffmail.com; Fax : 91-0133-452290

### ABSTRACT

Oxidation of pentane-1,5-diol, butane-2,3-diol and 2-methylpentane-2,4-diol by aqueous alkaline hexacyanoferrate (III) catalyzed by iridium trichloride shows first order kinetics with respect to hexacyanoferrate (III) at lower concentrations, which tends to be zero order at its higher concentrations. Reaction through out shows first order with respect to pentane-1,5-diol and 2-methyl pentane-2,4-diol concentrations while in case of butane-2,3-diol after showing first order kinetics initially, it becomes zero order at its higher concentrations. The kinetic behaviour with respect to hydroxide ion in case of 2-methyl pentane-2,4-diol is of first order. The order changes from one to zero at higher hydroxide concentrations for pentane-1,5-diol and butane-2,3-diol. The reaction mechanism through complex formation has been proposed.

**Key words :** Kinetic study, Oxidation, Hexacyanoferrate (III), Iridium trichloride, Diols.

### INTRODUCTION

Kinetics of oxidation of organic compounds by hexacyanoferrate (III) [referred as Hcf (III)] has been studied from time to time with and without the use of metal salts as catalyst<sup>1-4</sup>. Salts of osmium, ruthenium and rhodium are the most widely used catalyst in acidic and alkaline media. It has been observed by Singh and co-workers that iridium trichloride is also an effective catalyst for the oxidation of organic compounds in alkaline medium<sup>5,6</sup>. However, the use of iridium (III) chloride in the oxidation of diols is very limited. Thus, in order to collect more information about the mechanism of oxidation of diols by Hcf (III) in presence of iridium (III) chloride pentane-1,5-diol, 2-methylpentane-2,4-diol and butane-2,3-diol (referred as PD, MPD and BD respectively) have been selected as substrate.

### EXPERIMENTAL

Aqueous solution of pentane-1,5-diol, butane-2,3-diol and 2-methylpentane-2,4-diol (AnalaR) were prepared afresh. Solution of iridium trichloride (Johnson Mattay) was prepared

in very dilute solution of hydrochloric acid. The final strength of iridium trichloride was kept at  $2.83 \times 10^{-3}$  M. NaOH and potassium ferricyanide (AnalaR) were used and prepared in double distilled water. The ionic strength of the system was kept constant by using potassium chloride (E. Merck). The progress of the reaction was followed by estimating the amount of Hcf (III) ion produced after a definite time interval with a solution of ceric (IV) sulphate using ferroin as redox indicator<sup>7</sup>. The final oxidation products were identified by paper chromatographic and

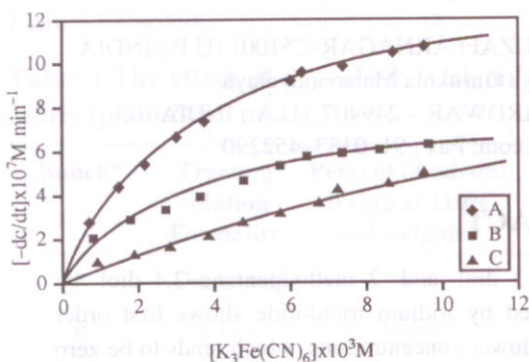


Fig. 1: Effect of  $[K_3Fe(CN)_6]$  on the reaction rate : (A)  $[PD] = 0.12M$ ,  $[NaOH] = 0.12M$ ,  $[IrCl_3] = 5.66 \times 10^{-5} M$ ,  $\mu = 0.25M$ , Temp. =  $35^\circ C$ . (B)  $[BD] = 0.20M$ ,  $[NaOH] = 0.18M$ ,  $[IrCl_3] = 5.66 \times 10^{-5} M$ ,  $\mu = 0.25M$ , Temp. =  $35^\circ C$ . (C)  $[MDP] = 0.10M$ ,  $[NaOH] = 0.20M$ ,  $[IrCl_3] = 5.66 \times 10^{-5} M$ ,  $\mu =$

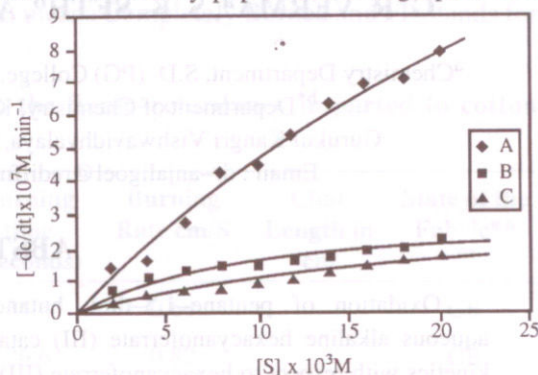


Fig. 2: Effect of Substrate on the reaction rate : (A)  $[PD]$ : Hcf (III) =  $2.5 \times 10^{-3} M$ ,  $[NaOH] = 0.10 M$ ,  $[IrCl_3] = 5.66 \times 10^{-5} M$ ,  $\mu = 0.25M$ , Temp. =  $35^\circ C$ . (B)  $[BD]$ : Hcf (III) =  $2.5 \times 10^{-3} M$ ,  $[NaOH] = 0.2M$ ,  $[IrCl_3] = 5.66 \times 10^{-5} M$ ,  $\mu = 0.25M$ , Temp. =  $35^\circ C$ . (C)  $[MPD]$ : (III) =  $2.0 \times 10^{-3} M$ ,  $[NaOH] = 0.15M$ ,

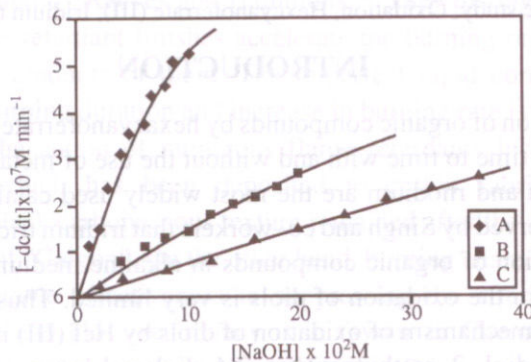


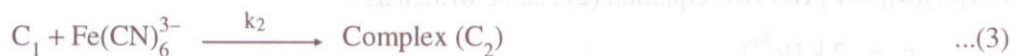
Fig. 3: Effect of  $[OH^-]$  on the reaction rate : (A)  $[PD] = 0.1M$ , Hcf (III) =  $2.5 \times 10^{-3} M$ ,  $[IrCl_3] = 5.66 \times 10^{-5} M$ ,  $\mu = 0.25M$ , Temp. =  $35^\circ C$ . (B)  $[BD] = 0.10 M$ , Hcf (III) =  $2.5 \times 10^{-3} M$ ,  $[IrCl_3] = 5.66 \times 10^{-5} M$ ,  $\mu = 0.25M$ , Temp. =  $35^\circ C$ . (C)  $[MPD] = 0.08 M$ , Hcf (III) =  $2.0 \times 10^{-3} M$ ,  $[IrCl_3] = 5.66 \times 10^{-5} M$ ,  $\mu = 0.5M$ , Temp. =  $40^\circ C$ .

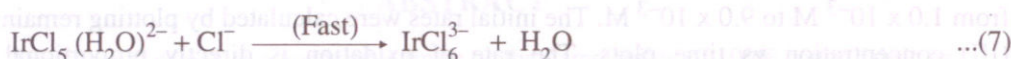
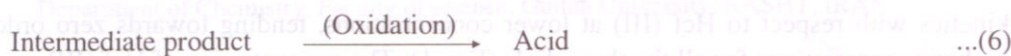
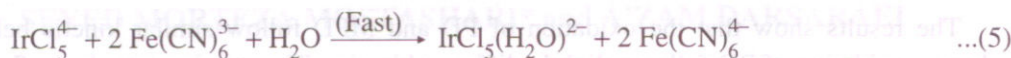
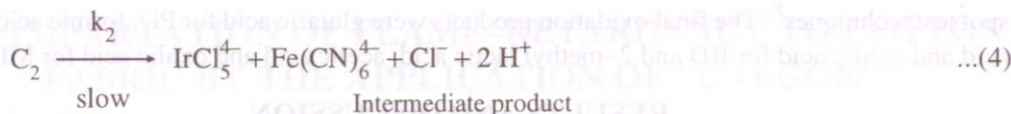
spot test techniques<sup>8</sup>. The final oxidation products were glutaric acid for PD, formic acid, acetic acid and oxalic acid for BD and 2-methyl lactic acid, acetic acid and oxalic acid for MPD.

## RESULTS AND DISCUSSION

The results show that the oxidation of PD and MPD follow similar kinetic behaviour whereas oxidation of BD follows slightly different kinetics. The reaction rate shows first order kinetics with respect to Hcf (III) at lower concentrations, tending towards zero order at its higher concentrations for all the three diols (Fig. 1). The concentration of Hcf (III) was varied from  $1.0 \times 10^{-3}$  M to  $9.0 \times 10^{-3}$  M. The initial rates were calculated by plotting remaining Hcf (III) concentration vs time plots. The rate of oxidation is directly proportional to the concentration of PD, BD and MPD but in case of BD at higher concentrations, it tends to be independent of substrate (BD) concentration.  $R^2$  values for curve A and C are 0.9853 and 0.9723, respectively. The concentration of substrates (PD, MPD and BD) were varied from  $1.0 \times 10^{-2}$  to  $10.0 \times 10^{-2}$  M (Fig. 2). The relationship between hydroxide ion concentration and reaction rate has been shown in Fig. 3. The figure clearly shows that the reaction follows first order kinetics at lower hydroxide concentrations which tends to be zero order at his higher concentrations in case of PD and some what in case of BD. For MPD, the reaction follows first order kinetics for many fold variation of hydroxide ion concentration. The hydroxide ion concentration was varied from  $1.0 \times 10^{-2}$  M to  $10 \times 10^{-2}$  M for PD. In case of BD and MPD, hydroxide concentration was varied from  $4.0 \times 10^{-2}$  to  $20.0 \times 10^{-2}$  M and  $2.0 \times 10^{-2}$  to  $36.0 \times 10^{-2}$  M, respectively. The order of reaction with respect to iridium trichloride is unity for many fold variation of its concentration in case of all the three organic substrates. The regression coefficient value  $R^2$  is 0.9936, 0.9972 and 0.9951 for PD, BD and MPD, respectively. The  $\text{IrCl}_3$  concentration was varied from  $1.415 \times 10^{-5}$  to  $0.490 \times 10^{-5}$  M. The ionic strength of the reaction mixture has a direct relationship with the rate of reaction (Positive salt effect). The temperature effect has been studied for the iridium (III) chloride catalysed oxidation of the above said diols. The observations have been made under identical conditions at different temperatures ranging from  $35^\circ\text{C}$ ,  $40^\circ\text{C}$ ,  $45^\circ\text{C}$  and  $55^\circ\text{C}$  by taking two specific runs for each of the diols. The values of energy of activation ( $E_a$ ) for the oxidation of PD, Bd and MPD are calculated, which are 11.90, 3.27 and 6.86 K Cals.  $\text{mole}^{-1}$ , respectively. These values indicates fastest oxidation of BD amongst the three diols.

The results given above clearly led us to propose the following reaction path-





Where 'S' represents organic substrate. The formation of anion of organic substrate in step (1) is supported by the fact that an alkoxide ion is formed when an alcohol is oxidised by alkaline potassium permanganate. It is assumed that the anion of organic substrate and  $\text{Ir}^{3+}$  forms a loosely bonded complex  $C_1$ , which combines with Hcf (III) to give another complex  $C_2$ . This complex  $C_2$  slowly disproportionates into  $\text{Ir}^I$  and  $\text{Fe}(\text{CN})_6^{4-}$  along with intermediate product. Intermediate product is further oxidised to give the final product (acid).  $\text{Ir}^I$  is reoxidised by two molecules of Hcf (III) via one electron transfer process. It is reported<sup>(10,11)</sup> that iridium trichloride exist as  $\text{IrCl}_6^{3-}$  in acid medium.  $\text{Ir}^{III}$  and  $\text{Ir}^I$  are the stable species of iridium.

The rate of reaction 'r' is measured in term of rate of disappearance of Hcf (III). According to step (3) rate of reaction will be—

$$r = -\frac{d \text{Hcf (III)}}{dt} = k_2 [C_2] \quad \dots(1)$$

At steady state and with the help of above proposed mechanism, the rate of disappearance of ferricyanide is given as —

$$r = -\frac{d \text{Hcf (III)}}{dt} = \frac{2 k K K_1 K_2 \text{Hcf (III)} [\text{Ir}^{3+}]_t [\text{S}] [\text{OH}^-]}{1 + K K_1 [\text{S}] [\text{OH}^-] + K K_1 K_2 [\text{S}] [\text{OH}^-] \text{Hcf (III)}} \quad \dots(2)$$

On the basis of experimental results at low concentrations of Hcf (III), organic substrate and hydroxide ion  $1 \gg K K_1 [\text{S}] [\text{OH}^-] + [K K_1 K_2] [\text{S}] [\text{OH}^-] \text{Hcf (III)}$  and equation (2) reduces to

$$r = 2 k_2 K K_1 K_2 \text{Hcf (III)} [\text{Ir}^{3+}]_t [\text{S}] [\text{OH}^-] \quad \dots(3)$$

Equation (3) clearly accounts for the first order kinetics with respect to Hcf (III), substrate, hydroxide ion and catalyst at their low concentrations. At higher concentrations,  $1 \ll K K_1 K_2 [\text{S}] [\text{OH}^-] \text{Hcf (III)}$  equation (2) can be written as —

$$r = 2 k [\text{Ir}^{3+}]_t \quad \dots(4)$$

i.e. the rate of reaction becomes independent of Hcf (III), substrate and hydroxide ion concentrations. However, it follows first order kinetics with respect to  $[\text{Ir}^{3+}]_t$ . The validity of proposed rate law might be ensured by rewriting the equation (2) as –

$$\frac{1}{r} = \frac{1}{2kKK_1K_2\text{Hcf(III)}[\text{Ir}^{3+}]_t[\text{S}][\text{OH}^-]} + \frac{1}{2kK_2\text{Hcf(III)}[\text{Ir}^{3+}]_t} + \frac{1}{2k[\text{Ir}^{3+}]_t} \dots(5)$$

The plots of  $1/r$  vs  $1/[\text{S}]$ ,  $1/[\text{OH}^-]$  and  $1/[\text{Ir}^{3+}]_t$  have been plotted for all the three diols. Straight lines with positive intercepts at  $1/r$  axis were obtained. The  $k$  values calculated from the intercept of plots for PD, BD and MPD are  $1.74 \times 10^{-2}$ ,  $5.78 \times 10^{-3}$ ,  $6.77 \times 10^{-3}$ , respectively.  $kK_1K_2$  values calculated from the slope are  $2.62 \times 10^2$ ,  $0.60 \times 10^2$  and  $0.22 \times 10^2$  for PD, BD and MPD, respectively.

### REFERENCES

1. A. E. Mucientes, F. J. Poblete, F. Santiago and J. Casado, *React. Kinet. Catal.*, **62**, 293 (1997).
2. H. S. Singh, G. R. Verma, Arti Gupta and Anjali Goel, *J. Indian Chem. Soc.*, **76**, 392 (1999).
3. A. Mucients Balado, F. Santiago Jimenz, F. J. Poblete Martin and R. Vaon Castellanos, *Int. J. Chem. Kinet.*, **29**, 1 (1997).
4. M. P. Singh, P. K. Tandon, Alka Mehrotra, Arti Gupta, J. P. Singh and V. S. Singh, *J. Indian Chem. Soc.*, **67**, 424 (1990).
5. Anjali Goel, G. R. Verma and H. S. Singh, *J. Indian Chem. Soc.*, **79**, 665 (2002).
6. S. K. Seth, Anjali Goel, G. R. Verma and H. S. Singh, *Asian J. Chem.*, **13**, 505 (2001).
7. V. N. Singh, H. S. Singh and B. B. L. Saxena, *J. Amer. Chem. Soc.*, **91**, 2643 (1960).
8. F. Fiegl, "Spot Tests in Organic Analysis," Elsevier New York, (1960) p. 809.
9. R. Stewart, *J. Amer. Chem. Soc.*, **79**, 2057 (1957).
10. J. C. Chang and C. S. Garner, *Inorg. Chem.*, **4**, 209 (1965).
11. F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", Wiley Eastern, New Delhi (1976).

Accepted : 25.4.2005