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Iridium(III) Chloride Catalysed Oxidation of Propan-2-one by Hexacyanoferrate(III) in Aqueous Alkaline Medium

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The kinetic data show direct proportionality with respect to ferricyanide concentrations. The reaction rate is directly proportional to the substrate, OH^- ions and iridium(III) at lower concentrations, but at higher concentrations the rate becomes independent of the substrate, alkali and the catalyst concentrations. These data suggest the formation of an activated complex between the substrate and iridium(III). This complex with ferricyanide gives another complex C_2, which slowly decomposes into the univalent iridium(I) species and the intermediate products which in turn are further oxidised by ferricyanide ions into the subsequent steps.

TRANSITION metal ions of group VIII are very effective catalysts and are widely used as homogeneous and heterogeneous catalysts in the oxidation of organic compounds in acidic or alkaline medium. Osmium[1] and ruthenium[2] are the most widely used catalysts in acidic as well as in alkaline medium. Iridium has also been used as catalyst, but the oxidation of ketones using iridium trichloride as a homogeneous catalyst is still unknown. So in the present study we have carried out the oxidation of propan-2-one by hexacyanoferrate(III) in aqueous alkaline medium using iridium(III) chloride as a homogeneous catalyst.

Experimental

The solution of propan-2-one (AnalaR) was prepared by direct weighing of the sample. The solution of iridium(III) chloride (Johnson Matthay) was prepared by dissolving the sample in a solution of hydrochloric acid. The final strengths of acid and iridium(III) chloride were 2.74×10^{-3} and 3.342×10^{-5} *M*, respectively. Other chemicals used were either AnalaR or chemically pure. The temperature of the reaction was electrically thermostated with an accuracy of $\pm0.1°$. The progress of the reaction was measured at different intervals of time by estimating the amount of hexacyanoferrate(II) produced with a standard solution of ceric sulphate using ferroin as indicator.

Results and Discussion

Iridium(III) chloride catalysed oxidation of propan-2-one was studied under the conditions where the uncatalysed reaction was negligible. The results are given in Table 1 and Figs. 1-4.

Table 1 indicates a gradual increase in $-dc/dt$ values which shows that the reaction rate is directly proportional with respect to ferricyanide concentrations. This nature is also clear from Fig. 1(A). Fig. 1(B) reveals that the reaction rate shows direct proportionality with respect to the lower concentrations of iridium(III) chloride, but the rate becomes independent of concentration at higher concentrations of the catalyst.

TABLE 1—EFFECT OF VARIATION OF HEXACYANOFERRATE(III) CONCENTRATION ON REACTION RATE AT 30°

$[NaOH]=10.0\times10^{-3}$ *M*, $[IrCl_3]=10.02\times10^{-5}$ *M*, Temp.$=30°$, $\mu=0.50$, [Propan-2-one]$=8.0\times10^{-3}$ *M*

$[K_3Fe(CN)_6]$ ($\times10^3$ *M*)	1.00	1.50	2.00	2.50	3.00	4.00	5.00	8.00
$-dc/dt$ ($\times10^5$ *M* min^{-1})	2.50	2.60	3.00	4.00	4.50	7.40	8.33	13.33

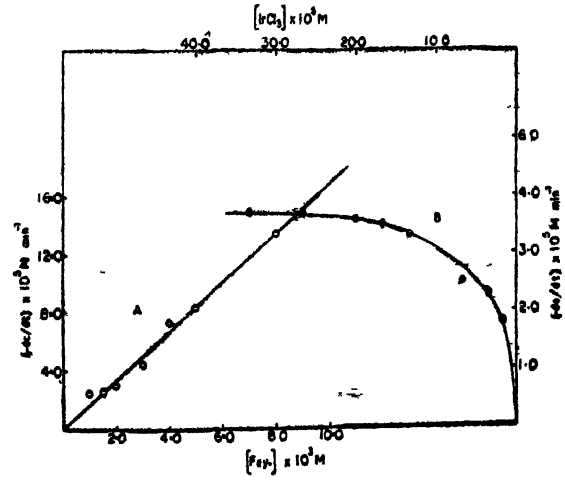

Fig. 1. Effect of variation of (A) [Ferricyanide] and (B) $[IrCl_3]$ on the reaction rate at 30 ; (A) $[NaOH]=10.0\times10^{-3}$ *M*, [Acetone]$=8.0\times10^{-3}$ *M*, $[IrCl_3]=10.02\times10^{-5}$ *M*, $\mu=0.50$ *M* ; and (B) $K_3Fe(CN)_6=2.0\times10^{-3}$ *M*, $[NaOH]=10.0\times10^{-3}$ *M*, [Acetone]$=8.0\times10^{-3}$ *M*, $\mu=0.50$ *M*.

Fig. 2 (A and B) shows first order kinetics at lower propan-2-one and NaOH concentrations,

but the reaction rate tends to become zero order at higher substrate and alkali concentrations.

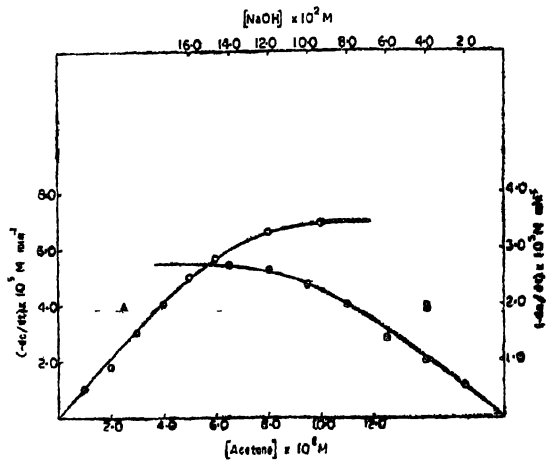

Fig. 2. Effect of variation of (A) [Acetone] and (B) [NaOH] on the reaction rate at 30°; (A) $[K_3Fe(CN)_6]=2.0\times10^{-3}$ *M*, $[NaOH]=10.0\times10^{-2}$ *M*, $[IrCl_3]=10.02\times10^{-5}$ *M*, $\mu=0.50$ *M*; and (B) $[K_3Fe(CN)_6]=2.0\times10^{-3}$ *M*, $[Acetone]=3.0\times10^{-3}$ *M*, $[IrCl_3]=10.02\times10^{-5}$ *M*, $\mu=0.50$ *M*.

After the completion of the reaction the final oxidation products were identified with tlc and spot test methods[8]. Appearance of red and blue colours by using appropriate reagents confirm the presence of oxalic acid and acetic acid, respectively as the final oxidation products in the oxidation of propan-2-one[4,11].

On the basis of the above results following rate expression might be proposed at lower concentrations of the substrate, alkali, catalyst and ferricyanide.

$$-\frac{d[Fey]}{dt}=k[S][OH][Ir^{III}][Fey] \qquad (1)$$

where, [S]=concentration of the substrate, [Fey] $=[Fe(CN)_6]^{3-}$ and k is the rate constant.

It is known[5] that $IrCl_3$ in hydrochloric acid medium gives $IrCl_6^{3-}$ species. It has also been reported that Ir(III) and Ir(I) ions are the stable species[6] of iridium and there is no evidence of the formation of Ir(II) species in the literature. Further, the aquation of $[IrCl_6]^{3-}$ gives $[IrCl_5(H_2O)]^{2-}$, $[IrCl_4(H_2O)_2]^-$ and $IrCl_3(H_2O)_3$ species[7,8] as shown by the following equation

$$IrCl_6^{3-}+nH_2O \rightleftharpoons [IrCl_{6-n}(H_2O)_n]^{3-n}$$

Since no retarding effect of Cl^- ions was observed hence the hydrated species cannot be the reactive species. Thus, $[IrCl_6]^{3-}$ has been considered as the only reactive species of $IrCl_3$ in the present study.

Thus, on the basis of the above results the probable pathway for the oxidation of propan-2-one might be described as follows.

$$S+OH^- \overset{K_1}{\rightleftharpoons} S^-+H_2O \qquad (i)$$

$$S^-+Ir^{3+} \overset{K_2}{\rightleftharpoons} (Complex)_1 \qquad (ii)$$

$$(Complex)_1+[Fey] \underset{C_1}{\overset{K_3}{\rightleftharpoons}} (Complex)_2 \qquad (iii)$$

$$(Complex)_2 \underset{C_2}{\xrightarrow[slow]{k}} IrCl_6^{4-}+Intermediate\ products+Cl^- \qquad (iv)$$

$$IrCl_6^{4-}+2Fe(CN)_6^{3-}+H_2O \xrightarrow[fast]{} [IrCl_5(H_2O)]^{2-}+2Fe(CN)_6^{4-} \qquad (v)$$

$$Intermediate\ products \xrightarrow[fast]{Oxid} \begin{matrix}COOH\\|\\COOH\end{matrix}+CH_3COOH \qquad (vi)$$

$$[IrCl_5(H_2O)]^{2-}+Cl^- \xrightarrow[fast]{} Ir^{3+}+H_2O \qquad (vii)$$

According to the above scheme enolate ion[1] with $IrCl_6^{3-}$ forms complex C_1 which again combines with ferricyanide to give another complex[9,10] C_2. This complex C_2 then slowly decomposes into the intermediate products and Ir^I species, which quickly gets oxidised by ferricyanide ions to $[IrCl_5(H_2O)]^{2-}$ species. The first oxidation products are further oxidised to give the final oxidation products; and $[IrCl_5(H_2O)]^{2-}$ species by taking Cl^- gives back the Ir^{III} species. The formation of the complexes C_1 and C_2 is confirmed by the plots of 1/rate *vs* 1/[substrate], and 1/[NaOH] and 1/[catalyst]. Straight lines with positive intercepts confirm the formation of the complexes[11]. Nature of the plot obtained in the substrate variation, *i.e.* direct proportionality of the reaction rate at lower concentrations of substrate which becomes independent with respect to the higher concentrations of substrate, itself confirms the complex formation between the substrate and the catalyst. Spectroscopic evidences for the formation of above complexes could not be provided because of the very short life of the complexes and due to the interference produced by the substrate and other reactants. Moreover, the results obtained, can be explained very accurately by the above mechanism.

From the above mechanism the concentrations of C_1, C_2 and ferricyanide can be given as

$$[C_1]=K_2[S^-][Ir] \qquad (2)$$

$$[C_2]=K_3[C_1][Fey] \qquad (3)$$

$$\text{and } [Fey]=\frac{[C_2]}{K_3[C_1]} \qquad (4)$$

The total concentration of ferricyanide can be given as

$$[Fey]_T=\frac{C_2}{K_3C_1}+C_2 \qquad (5)$$

At steady state condition, with the help of equations (2) to (5), the rate of disappearance of ferricyanide can be given as

$$V_i = -\frac{d[Fey]}{dt} = \frac{kK_1K_2K_3[S][OO^-][Ir^{III}][Fey]_T}{1+K_1K_2K_3[S][OO^-][Ir^{III}]} \quad (6)$$

Equation (6) clearly explains the nature shown by ferricyanide, substrate, hydroxide ions and iridium(III) chloride.

On the basis of the experimental results at low concentrations, one might safely assume that the value of $K_1K_2K_3[S][OH^-][Ir^{III}]$ will be quite small as compared to unity and the inequality, $1 \gg K_1K_2K_3[S][OH^-][Ir^{III}]$ will hold good. Thus equation (6) reduces to

$$-\frac{d[Fey]}{dt} = K_1K_2K_3[S][OH^-][Ir^{III}][Fey]_T \quad (7)$$

Equation (7) explains well the direct proportionality of the reaction rate with respect to lower concentrations of the substrate, hydroxide ions, iridium(III) and ferricyanide.

At higher concentrations, the reverse $1 \ll K_1K_2K_3[S][OH^-][Ir^{III}]$ will hold good and equation (6) becomes

$$-\frac{d[Fey]}{dt} = k[Fey]_T \quad (8)$$

Equation (8) clearly explains the first order kinetics with respect to ferricyanide even upto its many fold variations. This also explains that at higher concentrations, the rate will become independent with respect to the substrate, OH^- and iridium(III) concentrations.

The validity of the rate law might be made by rewriting equation (6) as

$$1/V_i = \frac{1}{k\,K_1K_2K_3[S][OH^-][Ir^{III}][Fey]_T} + \frac{1}{k[Fey]_T} \quad (9)$$

The plots of 1/rate *vs* 1/[S] and 1/[OH] and $1/[Ir^{III}]$ give straight lines with positive intercepts at $1/V_i$ axes (Figs. 3 and 4). With the help of the intercepts of 1/[S], 1/[OH] and $1/[Ir^{III}]$, k values were calculated to be 4.16×10^{-3}, 4.16×10^{-3} and 4.0×10^{-3}, respectively. Straight lines with positive intercepts and constant k values from three different slopes clearly confirm the validity of the rate law (equation 6) and the proposed mechanism.

Further, K_1, K_2 and K_3 values were calculated with the help of the slopes from the plots of 1/rate *vs* 1/[S], 1/[OH^-], and $1/[Ir^{III}]$ (Figs. 3 and 4), and these values come out to be 3.7×10^5, 12.1×10^5 and 14.5×10^5, respectively. The degree of agreement in K_1, K_2 and K_3 values calculated from three different plots again confirms the validity of rate law (equation 5).

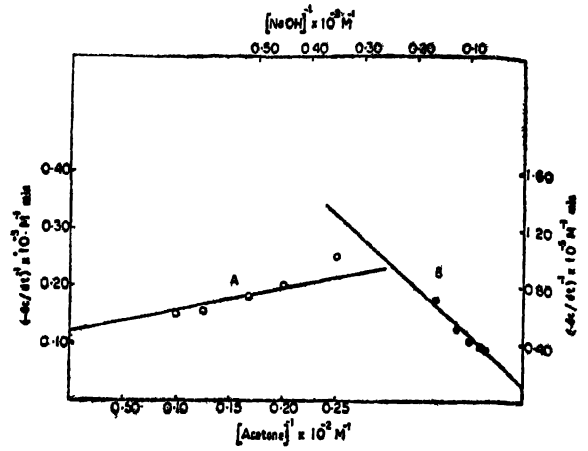

Fig. 3. Plots of 1/rate *vs* (A) 1/[Acetone] and (B) 1/[NaOH]; (A) $[K_3Fe(CN)_6]=2.0\times10^{-3}$ *M*, $[NaOH]=10.0\times10^{-3}$ *M*, $[IrCl_3]=10.02\times10^{-5}$ *M*, $\mu=0.50$ *M*; and (B) $[K_3Fe(CN)_6]=2.0\times10^{-3}$ *M*, [Acetone]$=3.0\times10^{-3}$ *M*, $[IrCl_3]=10.02\times10^{-5}$ *M*, $\mu=0.50$ *M*.

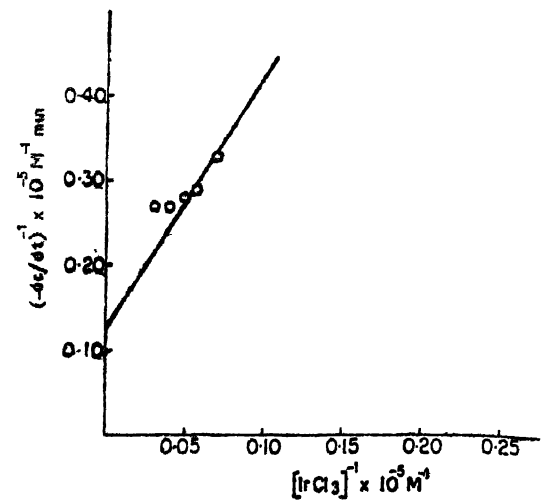

Fig. 4. Plots of 1/rate *vs* $1/[IrCl_3]$; $[K_3Fe(CN)_6]=2.0\times10^{-3}$ *M*, $[NaOH]=10.0\times10^{-3}$ *M*, [Acetone]$=3.0\times10^{-3}$ *M*, $\mu=0.50$ *M*.

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References

1. V. N. Singh, H. S. Singh and B. B. L. Saxena, *J. Am. Chem. Soc.*, 1969, **91**, 2643.
2. H. S. Singh, R. K. Singh, S. M. Singh and A. K. Sisodia, *J. Phys. Chem.*, 1977, **11**, 81.
3. F. Feigl, "Spot Tests Inorganic Chemistry", Elsevier, New York, 1960, pp. 369 86.
4. W. L. Evans and E. J. Witzemann, *J. Am. Chem. Soc.* 1912, **34**, 1096.

5. J. C. CHANG and C. S. GARNER, *Inorg. Chem.*, 1965, **4**, 209.
6. F. A. COTTON and G. WILKINSON, 'Advanced Inorganic Chemistry", Wiley Eastern Ltd., New Delhi, 1976, p. 434.
7. V. I. KRAVTSOV and G. M. PETROVA, *Russ. J. Inorg. Chem.* (*Engl. Transl.*), 1964, **9**, 552.
8. I. A. POULSEN and C. S. GARNER, *J. Am. Chem. Soc.*, 1962, **84**, 2032.
9. R. M. SINGH, Ph. D. Thesis, Allahabad University, 1981 ; D. K. SINGH, Ph. D. Thesis, Allahabad University, 1981.
10. H. C. GUPTA, Ph. D. Thesis, Meerut University, 1981.
11. L. MICHALIS and M. L. MENTEN, *Biochem. J.*, 1933, **49**, 333.