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# Kinetics of Oxidation of Hexacyanoferrate(II) By Peroxodiphosphate

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*Kinetic evidence for inner sphere oxidative path was observed in the oxidation of hexacyanoferrate(II) by peroxodiphosphate at pH = 10 and 26° C. The reaction obeys the rate law*

$$\frac{d[Fe(CN)_6^{3-}]}{dt} = \frac{k_tK[P_2O_8^{4-}][Fe(CN)_6^{4-}]_{total}}{[CN^-]^2 + K[P_2O_8^{4-}]}$$

*suggesting the mechanism*

$$Fe(CN)_6^{4-} + P_2O_8^{4-} \overset{K}{\rightleftharpoons} [Fe(CN)_4P_2O_8]^{6-} + 2\ CN^-$$

$$[Fe(CN)_4P_2O_8]^{6-} \xrightarrow[slow]{k_t} Products$$

*Added free ligand, CN⁻, effects a remarkable decrease in the reaction rate in accordance with the rate law. Effect of pH on the reaction rate was studied and evidence for free radical intermediates was obtained.*

## Introduction

Oxidation of a number of Fe(II) complexes by peroxodiphosphate, PP, was carried out by Edwards and coworkers[1–3]. It was observed that, in all these reactions, the rate-determining step was the dissociation of the Fe(II) complex and hence the kinetics exhibited zero-order dependence on PP. It is of interest to study the oxidation of $Fe(CN)_6^{4-}$, the dissociation constant of which is very small[4], to find out whether this complex also reacts by a similar mechanism as the other Fe(II) complexes with PP and to compare the results with those for the $Fe(CN)_6^{4-}$–$S_2O_8^{2-}$ system[5–8].

## Experimental

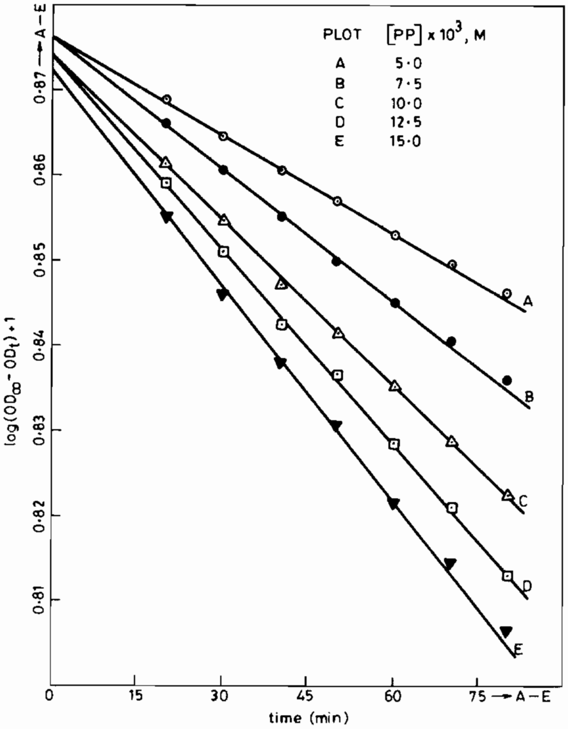
$K_4P_2O_8$ (FMC Corporation, U.S.A) was converted into $Li_4P_2O_8 \cdot 4H_2O$ and purified (99.1%) according to the method of Chulski[9]. $K_4Fe(CN)_6$, NaOH, $KH_2PO_4$, $Na_2HPO_4$ (AR, BDH), perchloric acid (60% GR, E. Merck) and other chemicals used were of analar grade. $LiClO_4$ and $NaClO_4$ were prepared by neutralising equinormal amounts of $Li_2CO_3$ and NaOH respectively with perchloric acid. Water used was doubly distilled over alkaline permanganate and deionized over Biodeminrolit (Permutit Co., U.K.) mixed-bed ion-exchange resin. All the preparations of reagents and solutions were done with this double distilled water. Phosphate buffers[10], $KH_2PO_4$ + NaOH (pH = 6 to 8) and $Na_2HPO_4$ + NaOH (pH = 9 to 10), were used to maintain a constant pH of the reaction medium.

All the experiments were carried out with $[PP] \gg [Fe(CN)_6^{4-}]$ at pH = 10 and at a constant ionic strength of 0.3*M*. The pH of the medium was also varied from 10 to 6 to find out the dependence of rate on pH at constant ionic strength. Formation of $Fe(CN)_6^{3-}$ was tested by addition of $Fe^{2+}$ which produced a blue colour and the kinetics were investigated spectrophotometrically by following the appearance of $Fe(CN)_6^{3-}$ at 420 nm[8] at room temperature (26° C) using a Hilger Uvispek H-700 instrument. $Fe(CN)_6^{4-}$ has negligible absorption at this wavelength. The pH of the medium was checked by pH meter (Leeds and Northrup Co., Philadelphia, U.S.A.) before and after the reaction. Calculated volumes of buffer solution, peroxodiphosphate ($5–15 \times 10^{-3}M$), $LiClO_4$ or $NaClO_4$ (to adjust the ionic strength) and water were pipetted out into a 100 ml flask and the reaction was started by adding $Fe(CN)_6^{4-}$ ($4–12 \times 10^{-4}M$). The reaction mixture was transferred immediately into a quartz cell ($1\ cm^2 \times 3$ cm) and the optical density (OD) was measured at 420 nm at known intervals of time. The final reading of optical density ($OD_\infty$) was taken after the complete disappearance of $Fe(CN)_6^{4-}$ by allowing the reaction to proceed for about 12 hours. ($OD_\infty - OD_t$) would be proportional to $[Fe(CN_6^{4-}]_t$ and k′ ($sec^{-1}$) was evaluated from the slopes of the plots of $\log(OD_\infty - OD_t)$ *vs.* time. The stoichiometry of the reaction, $-\Delta[Fe(CN)_6^{4-}]/-\Delta[PP]$ was established by taking $[Fe(CN)_6^{4-}] \gg [PP]$ and estimating the unreacted hexacyanoferrate(II) by permanganometry, since the unreacted peroxodiphosphate could not be determined under the usual experimental conditions ($[PP] \gg [Fe(CN)_6^{4-}]$).

## Results

The first order dependence on $[Fe(CN)_6^{4-}]$ was evident from the linear plots of log ($OD_\infty - OD_t$) *vs.*

time (Figure 1). The pseudo-first-order rate constants, k′ ($sec^{-1}$), evaluated from the slopes of the above plots, were found to be independent of the initial concentrations of hexacyanoferrate(II) (Figure 2). Plots of 1/k′ *vs.* 1/[PP] were linear with non-zero intercepts (Figure 3, Table I) indicating Michaelis–Menten kinetics[11]. Similar kinetic behaviour was observed indicating complex formation in oxidations involving metal ions[12,13] as oxidants. The difference lies in the fact that in the present study the oxidant functions as a ligand whereas with metal ions as oxidants, the substrate would be the ligand. The dissociation constant of the complex, $k_t$ ($sec^{-1}$), can be evaluated from the intercept of the plot of 1/k′ *vs.* 1/[PP] ($k_t$ = 1/intercept; Table I). Added $CN^-$ ($5–25 \times 10^{-6} M$) effected a pronounced decrease in the rate (Table II) and the plot of 1/k′ *vs.* $[CN^-]^2$ was found to be linear (Figure 3), showing the second order dependence on



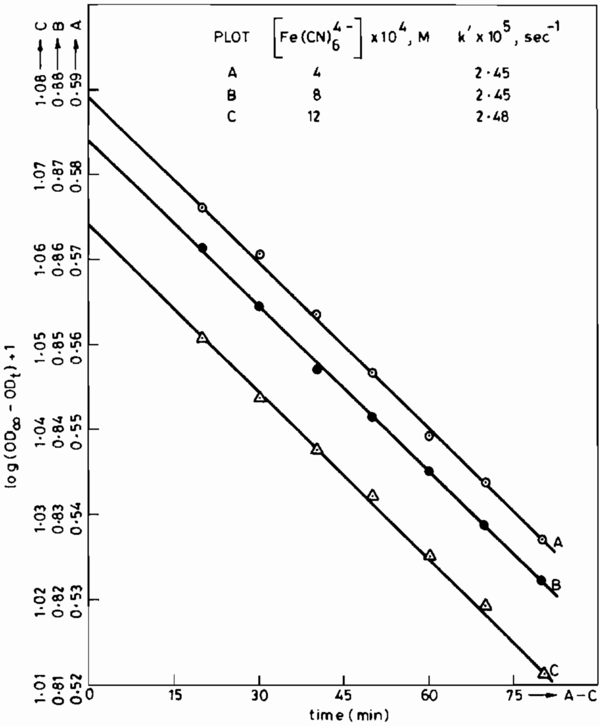


Figure 1. Plots showing the first order dependence on $[Fe(CN)_6^{4-}]$. $[Fe(CN)_6^{4-}] = 8 \times 10^{-4} M$, pH = 10, $\mu = 0.3 M$, *26° C and* $\lambda$ = 420 nm.

Figure 2. Plots showing the independence of k′ ($sec^{-1}$) on the initial concentrations of $Fe(CN)_6^{4-}$. [PP] = 0.01 *M*, pH = 10, $\mu = 0.3 M$, 26° C, $\lambda$ = 420 nm.

TABLE I. Michaelis–Menten Kinetics in the Oxidation of Hexacyanoferrate(II). pH = 10; Temp. = 26° C; $[Fe(CN)_6^{4-}] = 8 \times 10^{-4} M$; $\mu = 0.3 M$; $\lambda$ = 420 nm.

| $[PP]^{-1} \times 10^{-1}$, $M^{-1}$ | pH = 10 | pH = 7 |
|---|---|---|
| | 1/k′ × $10^{-4}$, sec | 1/k′ × $10^{-3}$, sec |
| 20.00 | 6.74 | 3.26 |
| 13.33 | 5.09 | 2.61 |
| 10.00 | 4.08 | 2.28 |
| 8.00 | 3.47 | 2.11 |
| 6.67 | 3.03 | 1.95 |
| | $k_t = 7.69 \times 10^{-5}$ $sec^{-1}$ | $k_t = 7.69 \times 10^{-4}$ $sec^{-1}$ |
| | $\frac{K}{[CN^-]^2} = 47.28$ | $\frac{K}{[CN^-]^2} = 132.9$ |

[$CN^-$]. It was also checked that there was no reaction between $CN^-$ and PP in a separate experiment. These observations clearly indicated the replacement of 2 $CN^-$ ligands by $P_2O_8^{4-}$ in the formation of the complex. The reaction was found to be pH dependent; lowering of pH from 10 to 6 enhanced the reaction rate (Table III). Michaelis–Menten kinetics were observed in the pH range 10 to 7 but at pH = 6 k′ ($sec^{-1}$) was found to be independent of [PP] (Table III). Moreover, at pH < 6 the reaction becomes immeasurably fast. The increase in rate with decreasing pH may be attributed to (i) the higher reactivity of the protonated species of both peroxodiphosphate and hexacyanoferrate(II) and (ii) the following equilibrium involving $CN^-$,

$$CN^- + H_2O \rightleftharpoons HCN + OH^- \qquad (1)$$

The effect of ionic strength by added $NaClO_4$ or $LiClO_4$ was found to be negligible. Initiation of vinyl polymerization by the $P_2O_8^{4-}$–$Fe(CN)_6^{4-}$ redox system indicated the formation of free radical intermediates. The stoichiometry of the reaction was estimated to be [$Fe(CN)_6^{4-}$] : [$P_2O_8^{4-}$] = 2 : 1.

## Discussion

Our kinetic observations are interesting in that they clearly indicate the operation of the inner sphere mechanism of oxidation. The active species of hexacyanoferrate(II)[14] and peroxodiphosphate[15] at pH =

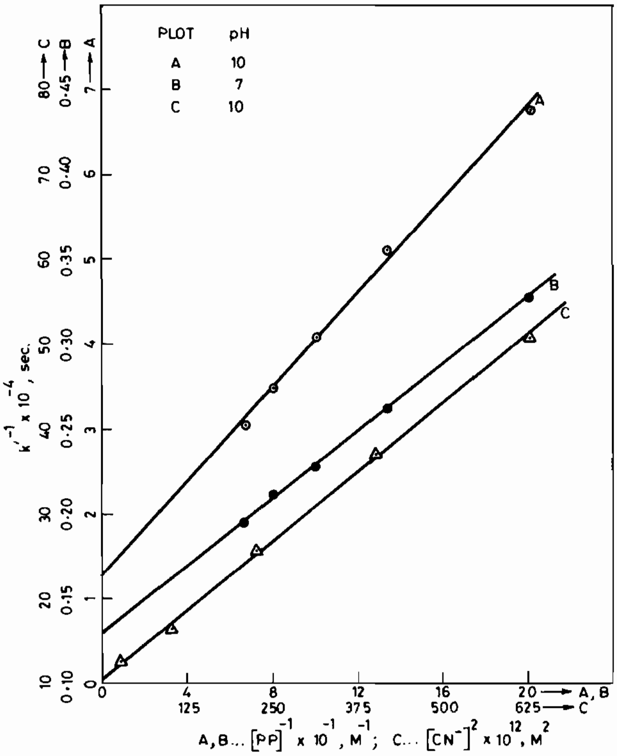


Figure 3. Michaelis–Menten plots and the inverse dependence of rate on $[CN^-]^2$ (experimental conditions as given in Tables I and II).

TABLE II. Effect of Added $CN^-$. pH = 10; $\mu = 0.3M$; Temp. = 26° C; [PP] = $0.01M$; [$Fe(CN)_6^{4-}$] = $8 \times 10^{-4}M$; $\lambda$ = 420 nm.

| [$CN^-$] × $10^6$, $M$ | k′ × $10^6$, $sec^{-1}$ | $[CN^-]^2 \times 10^{12}$, $M^2$ | 1/k′ × $10^{-5}$, sec |
|---|---|---|---|
| 5 | 8.08 | 25 | 1.24 |
| 10 | 6.14 | 100 | 1.63 |
| 15 | 3.92 | 225 | 2.55 |
| 20 | 2.70 | 400 | 3.70 |
| 25 | 1.98 | 625 | 5.05 |

TABLE III. Effect of pH. [$Fe(CN)_6^{4-}$] = $8 \times 10^{-4}M$; $\mu = 0.3M$; Temp. = 26° C; $\lambda$ = 420 nm.

| pH | k′ × $10^5$, $sec^{-1}$ | | | | |
|---|---|---|---|---|---|
| | [PP] = $5 \times 10^{-3}M$ | $7.5 \times 10^{-3}M$ | $10 \times 10^{-3}M$ | $12.5 \times 10^{-3}M$ | $15 \times 10^{-3}M$ |
| 10 | 1.48 | 1.97 | 2.45 | 2.88 | 3.30 |
| 9 | 8.60 | 10.51 | 12.43 | 13.51 | 14.33 |
| 8 | 12.15 | 14.79 | 16.21 | 17.40 | 18.56 |
| 7 | 30.71 | 38.39 | 43.86 | 47.45 | 51.18 |
| 6 | 221.40 | 221.40 | 221.40 | 221.40 | 221.40 |

10 would be $Fe(CN)_6^{4-}$ and $P_2O_8^{4-}$ since only the unprotonated species would be present at this alkaline pH. Since Michaelis–Menten kinetics were observed with inverse dependence of rate on $[CN^-]^2$, an inner sphere mechanism involving complex formation may be proposed as follows:

$$Fe(CN)_6^{4-} + P_2O_8^{4-} \overset{K}{\rightleftharpoons} \underset{\text{Complex}}{[Fe(CN)_4P_2O_8]^{6-}} + 2CN^- \quad (2)$$

$$[Fe(CN)_4P_2O_8]^{6-} \xrightarrow[\text{slow}]{k_t} \text{Products} \quad (3)$$

$$\text{Rate} = \frac{d[Fe(CN)_6^{3-}]}{dt} = k_t[\text{Complex}] \quad (4)$$

$$\text{Rate} = \frac{k_tK[P_2O_8^{4-}][Fe(CN)_6^{4-}]_{total}}{[CN^-]^2 + K[P_2O_8^{4-}]} \quad (5)$$

$$\frac{1}{k'} = \frac{[CN^-]^2}{k_tK[P_2O_8^{4-}]} + \frac{1}{k_t} \text{ since } k' = \frac{\text{Rate}}{[Fe(CN)_6^{4-}]_{total}}$$

The equilibrium constant, K, could not be evaluated from the slope and intercept of the plot of $1/k'$ *vs.* 1/[PP] because of the unknown value of $[CN^-]$ arising from the equilibrium reaction (2). Consequently it can be given only as a function of $[CN^-]^2$ (Intercept/Slope $= \frac{K}{[CN^-]^2}$; Table I).

The replacement of two $CN^-$ ligands by $P_2O_8^{4-}$ in the formation of the complex (PP functions as a bidentate ligand) as given by equation (2) is supported by the fact that $Fe(CN)_6^{4-}$ forms substitution complexes[16,17] of the type $Fe(CN)_4AA^{2-}$ where AA is a bidentate ligand like 1,10-phenanthroline, 2,2′-bipyridyl, *etc.* The inverse dependence of rate on $[CN^-]^2$ (Figure 2) observed in accordance with the rate law is in support of the formation of the complex, $[Fe(CN)_4P_2O_8]^{6-}$. Complex formation between PP and metal ions like $VO^{2+}$ [18] and a number of Fe(II) complexes[1–3] (actually $FeL_2^{2+}$) and the preponderance of inner sphere oxidative paths for peroxodiphosphate[2], already suggested by Edwards *et al.,* also support our mechanistic conclusions.

The reaction mechanism is not as simple as it appears to be. Equilibrium (2) should involve very complicated reactions as this $S_N2$ reaction involves the substitution of two monodentate ligands (2 $CN^-$) by a bidentate ligand, PP. Kinetic data could give information only about reactions (2) and (3) and their relative velocities. Of these two, reaction (3) is found to be the slow rate-determining one. Equilibrium (2) is rapidly achieved compared to the slow dissociation of the complex (equation 3) and it is not possible to find out the nature of the reversal of equilibrium (2) in the absence of K values. Since $[CN^-]^2$ would be very low ($< 10^{-6}$) under the present experimental conditions, $K/[CN^-]^2$ values (Table I) would indicate that the reverse reaction of equilibrium (2) would be more rapid than equilibrium (2) itself. Equilibrium (1) involving $CN^-$ would be operative in the pH range studied and hence the reverse of equilibrium (2) might involve HCN also. The decrease in rate with added $CN^-$ (Table II) and the second order dependence on $[CN^-]$ support the equilibrium suggested by us and such a rate-retarding effect by added free ligand has also been observed by Edwards *et al.*[1] in the oxidation of $Fe(Phen)_3^{2+}$ by PP. The dissociation of the complex (equation 3) would give rise to free radicals $\cdot PO_4^{2-}$. As the stoichiometry of the reaction $[Fe(CN)_6^{4-}]$:[PP] is found to be 2 : 1, the secondary reactions would include reactions of the type,

$$Fe(CN)_6^{4-} + \cdot PO_4^{2-} \rightarrow Fe(CN)_6^{3-} + PO_4^{3-}$$

It is of interest to compare the oxidation of $Fe(CN)_6^{4-}$ with that of the other Fe(II) complexes by peroxodiphosphate[1–3]. Under similar experimental conditions, [PP] $\gg$ [Fe(II) complex] and [PP] $> 2 \times 10^{-3}M$, the former reaction obeyed Michaelis–Menten kinetics involving the formation of a mixed-ligand complex between $Fe(CN)_6^{4-}$ and PP (equilibrium 2) whereas the latter reaction obeyed first order kinetics involving the dissociation of the Fe(II) complex as the rate-determining step[1–3]:

$$FeL_3^{2+} \underset{}{\overset{\text{slow}}{\rightleftharpoons}} FeL_2^{2+} + L$$

where L is a bidentate ligand. The rate law for the oxidation of hexacyanoferrate(II) is given by equation (5) while that for the oxidation of other Fe(II) complexes by PP is of the form:

$$\frac{-d[\text{Fe(II) complex}]}{dt} = k_{obs}[\text{Fe(II) complex}]$$

In both the cases, inner sphere mechanisms involving the formation of free radical ($\cdot PO_4^{2-}$) were suggested.

A comparison of the oxidation of hexacyanoferrate (II) by $P_2O_8^{4-}$ and $S_2O_8^{2-}$ showed that there is a wide disparity between the kinetics and mechanism of the two reactions. Kinetic evidence for complex formation (Michaelis–Menten kinetics) was obtained in the oxidation by PP indicating an inner sphere oxidative path whereas no such evidence was obtained in the oxidation by $S_2O_8^{2-}$ [5–8] suggesting an outer sphere mechanism to be operative.

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