Role of trace iron(III) and equilibrium $\text{Fe(III)} + \text{Fe(CN)}_6^{4-} \rightleftharpoons \text{Fe(II)} + \text{Fe(CN)}_6^{3-}$ in the investigation on kinetics and mechanism of oxidation of hexacyanoferrate(II) by peroxodiphosphate in acid perchlorate solution

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Received 6 May 1992; accepted 1 October 1992

Oxidation of hexacyanoferrate(II) with peroxodiphosphate (pdp) in aqueous perchloric acid solutions occurs through the catalysis by Fe(III) present in traces in the reagents and distilled water involving the equilibrium. $\text{Fe(III)} + \text{Fe(CN)}_6^{4-} \rightleftharpoons \text{Fe(II)} + \text{Fe(CN)}_6^{3-}$. Fe(II) is oxidised back to Fe(III) by pdp in the fast step. The rate law is $\frac{d[\text{Fe(CN)}_6^{3-}]}{dt} = \left( k_1 + \frac{k_2}{[H^+]} \right) [\text{Fe(III)}] [\text{Fe(CN)}_6^{4-}]$. The values of $k_1$ and $k_2$ have been found to be $5.7 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and $36 \text{ s}^{-1}$ respectively at $I = 0.5 \text{ mol dm}^{-3}$ and $30°$. The equilibrium constant for the above equilibrium determined spectrophotometrically is $34 \pm 4$ at $28°$, $I = 0.05 \text{ mol dm}^{-3}$ and $[H^+] = 0.01 \text{ mol dm}^{-3}$. Aquo copper(II) retards the rate of oxidation of Fe(CN)$_6^{3-}$ by pdp. Spectrophotometrically too the equilibrium is shifted to the left in the presence of Cu(II).

Trace metal ions of iron(III) and copper(II) which are commonly found in the reagents and distilled water greatly influence or rather monitor the kinetics of redox reactions, particularly when one of the reactants is peroxodiphosphate (pdp). The oxidations of ascorbic acid$^1$ in acetate buffers and that of hexacyanoferrate(II)$^2$ in acid perchlorate solutions have already been reported. The latter investigation gives a detailed study of the catalysis by Cu(II) edta complex with the following mechanism.

$$\text{Cu}^{II}(\text{edta})^2+ + \text{HFe(CN)}_6^{3-} \rightleftharpoons \text{Cu}^{II}(\text{edta})^3+ + \text{HFe(CN)}_6^{4-} \quad \ldots (1)$$

$$\text{Cu}^{II}(\text{edta})^3+ + \text{pdp} \rightarrow \text{Cu}^{II}(\text{edta}) + \text{products} \quad \ldots (2)$$

It was also reported that Fe(III)edta complex is not effective, but aqua Fe(III) is, but it is not known whether aqua Fe(III) also acts by a similar mechanism. A significant result of the previous study was the inhibition by aqua Cu(II) ions, though no details or mechanism were given. A similar inhibition by aqua Fe(III) was noticed in the Cu(II) catalysed reduction$^3$ by Fe(CN)$_6^{3-}$ by hydroxylamine, though Fe(III)edta complex catalyses the reaction. It was therefore worthwhile to know whether there is any correlation between the inhibition by aqua Cu(II) in the oxidation of Fe(CN)$_6^{4-}$, and inhibition by aqua Fe(III) in the reduction of Fe(CN)$_6^{3-}$. The present paper describes a kinetic study of the Fe(III) catalysed oxidation of hexacyanoferrate(II) by peroxodiphosphate in acid perchlorate solutions as well as in acetate buffers and the spectrophotometric determination of the equilibrium constant of the title reaction. Reduction$^3$ of Fe(CN)$_6^{3-}$ by hydroxylamine alone, studied earlier in phosphate and borate buffers, was reinvestigated in acetate buffers to lend support to the operation of the title equilibrium.

Materials and Methods

Solutions of tetrapotassium salt of potassium peroxide phosphate (pdp) (a gift sample from FMC Corporation, USA) were prepared by dissolving a known quantity of the salt in water whenever required and standardised iodometrically$^4,5$. Solutions of K$_5$Fe(CN)$_6$ (BDH, AnalR) were always freshly prepared, kept in a refrigerator to minimise deterioration or oxidation, and then strength determined iodimetrically$^5$. Iron(III) perchlorate (Fluka, AG) was determined by adding a known excess (about four times) of sodium thiosulphate, allowing time (1 min) for completion of reaction, and back titrating the excess thiosulphate with a standard solution of iodine. All other reagents were either BDH AnalR or E. Merck. Doubly distilled water, second distillation being from alkaline permanganate, was employed for preparing solutions and in the reaction mixture.

Kinetic procedure

The reactions were carried out in a conical flask
kept in a thermostat at 30°. The reaction was initiated by adding a known quantity of pdp to the other constituents of the reaction mixture, which were Fe(CN)$_3^{3-}$, Fe(III), HClO$_4$ and LiClO$_4$ of appropriate concentrations. Kinetics were followed by taking out aliquots (5 ml) at suitable intervals and adding to 5 ml of 1.0 mol dm$^{-3}$ NaOH to quench the reaction and determining Fe(CN)$_3^{3-}$ formed in the reaction mixture, colorimetrically at 420 nm ($\varepsilon = 1020 \pm 10$) on Spectronic 20 Bausch and Lomb spectrophotometer. Initial rates were determined by the plane mirror method. The results were reproducible within ±5%. Reactions were carried out in acetate buffers too, to show the inhibiting effect of Fe(CN)$_3^{3-}$. Reduction of Fe(CN)$_3^{3-}$ by hydroxylamine was also studied to show the inhibiting effect of Fe(CN)$_3^{3-}$ and operation of title equilibrium in backward direction.

Direct reaction of Fe(II) and pdp was carried out in acid perchlorate solutions at 5°C. The reaction was very fast to study by conventional methods.

**Spectrophotometry**

This work was done on CE 599 automatic scanning Cecil spectrophotometer to determine equilibrium constant of the reaction mentioned in the title. Absorbances were measured at 220 nm at 28°, [HClO$_4$] = 0.01 mol dm$^{-3}$ and I = 0.05 mol dm$^{-3}$ adjusted with LiClO$_4$. The concentrations of the reactants Fe(III), Fe(CN)$_3^{3-}$, Fe(II) and Fe(CN)$_3^{3-}$ were in the range of 1 x 10$^{-6}$ to 1 x 10$^{-5}$ mol dm$^{-3}$. Fe(III), Fe(CN)$_3^{3-}$ and Fe(CN)$_3^{3-}$ absorb at 220 nm with $\varepsilon$ (dm$^3$ mol$^{-1}$ cm$^{-1}$) of 3140, 16430 and 6000 respectively and Fe(II) does not absorb at this wavelength. Absorbances of the mixtures were also reported at different [H$^+$] but fixed concentrations of other reactants. The results are reproducible if [HClO$_4$] and [LiClO$_4$] are less than 0.05 mol dm$^{-3}$. Equilibrium is reached in less than a minute. Concentrations of the reagents were small enough to result in any significant anion-cation association except protonation of Fe(CN)$_3^{3-}$. A blue colour appeared, but only after 20 min and hence there was no complication for spectrophotometric measurements.

The equilibrium constant K was calculated from the observed absorption (A) and the molar extinction coefficients of various species at 220 nm and was found to be 34 ± 4 at I = 0.05 mol dm$^{-3}$ and 28°. Approach to equilibrium was made from both the directions. These results are given in Table 1.

For investigating the effect of [H$^+$], the measurements were made at [HClO$_4$] = 0.02, 0.03, 0.04 and 0.05 mol dm$^{-3}$ at fixed I = 0.05 mol dm$^{-3}$. Values of K did not change in the [H$^+$] range investigated. Although the average deviation was not larger than 12%, the individual values differed to the extent of 50% from the average value. The results were less accurate when the difference in the concentrations of the two reactants Fe(III) and Fe(CN)$_3^{3-}$ or Fe(II) and Fe(CN)$_3^{3-}$ was larger than that shown in Table 1. Results were more scattered if equilibrium was approached by initially starting with Fe(III) and Fe(CN)$_3^{3-}$.

**Results**

**Stoichiometry**

Stoichiometric determinations with various combinations of the concentrations of the reactants and

<table>
<thead>
<tr>
<th>[HClO$_4$] mol dm$^{-3}$</th>
<th>$10^6$ [Fe(III)]$_b$ mol dm$^{-3}$</th>
<th>$10^6$ [Fe(CN)$_3^{3-}$]$_b$ mol dm$^{-3}$</th>
<th>$10^6$ [Fe(II)]$_b$ mol dm$^{-3}$</th>
<th>$10^6$ [Fe(CN)$_3^{3-}$]$_b$ mol dm$^{-3}$</th>
<th>A</th>
<th>K</th>
</tr>
</thead>
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<td>4.0</td>
<td>5.0</td>
<td>-</td>
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<td>0.045</td>
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<tr>
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<tr>
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<td>-</td>
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<td>0.040</td>
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<td></td>
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<tr>
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<td>-</td>
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<td>0.041</td>
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<td></td>
</tr>
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<td>-</td>
<td>-</td>
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<td>0.042</td>
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<td>5.0</td>
<td>0.043</td>
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</tr>
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<td>-</td>
<td>5.0</td>
<td>5.0</td>
<td>0.041</td>
<td>27</td>
<td></td>
</tr>
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</table>
Fe(CN)$^{6-}_{6}$ being in excess, yielded a value of $\Delta[\text{Fe(CN)}^{6-}_{6}]/\Delta[pdp] = 2.00 \pm 0.02$. Fe(CN)$^{6-}_{6}$ was measured as described. The reaction appears to occur as in Eq. (3).

$$2 \text{Fe(CN)}^{6-}_{6} + \text{H}_4\text{P}_2\text{O}_6 + 2\text{H}^+ \rightarrow 2\text{Fe(CN)}^{3-}_{3} + 2\text{H}_3\text{PO}_4 \quad \ldots (3)$$

Effect of Fe(III) and edta

The rate increases with the increase of [Fe(III)] as given in Fig. 1. The intercept on the rate axis indicates that the uncatalysed reaction also occurs. However, in reality it is not 'uncatalysed'. The intercept is obtained on account of the iron(III) present as impurity in the reagents and distilled water. Atomic absorption of the reaction mixture containing [pdp] = 1.0 x 10$^{-3}$ mol dm$^{-3}$, [Fe(CN)$^{6-}_{6}$] = 1.0 x 10$^{-3}$ mol dm$^{-3}$, [HClO$_4$] = 0.01 mol dm$^{-3}$ and [LiClO$_4$] = 0.04 mol dm$^{-3}$, showed the presence of approximately 3 x 10$^{-7}$ mol dm$^{-3}$ of Fe(III). The slope of the line of Fig. 1 is 6.5 s$^{-1}$ and hence the expected uncatalysed (really catalysed) rate would be (3 x 10$^{-7}$ x 6.5) = 1.95 x 10$^{-6}$ dm$^3$ mol$^{-1}$ s$^{-1}$. This is close to the value of 2.1 x 10$^{-6}$ dm$^3$ mol$^{-1}$ s$^{-1}$ (Fig. 1). This confirms that the oxidation of Fe(CN)$^{6-}_{6}$ by pdp mainly operates through catalysis by Fe(III). The rate drastically decreased in the presence of edta. For example, under the conditions [pdp] = 1 x 10$^{-3}$ mol dm$^{-3}$, [Fe(CN)$^{6-}_{6}$] = 1.0 x 10$^{-2}$ mol dm$^{-3}$, [HClO$_4$] = 0.05 mol dm$^{-3}$ and I = 0.5 mol dm$^{-3}$, 10$^6$ (initial rate) decreased from 39 to 1.0 mol dm$^{-3}$ s$^{-1}$ at 35°C and from 15 to 0.1 mol dm$^{-3}$ s$^{-1}$ at 25°C when 10$^3$ [edta] was varied from 0 to 10.0 mol dm$^{-3}$. This further proves that some metal ion present in the system monitors the rate of Fe(CN)$^{6-}_{6}$-pdp reaction and that its effect is masked owing to strong complexing of the metal ions with edta.

**Peroxodiphosphate dependence**

The [pdp] was varied in the range (5 x 10$^{-4}$ to 1 x 10$^{-2}$) mol dm$^{-3}$ at fixed [Fe(CN)$^{6-}_{6}$] = 1.0 x 10$^{-3}$ mol dm$^{-3}$, added [Fe(III)] = 5 x 10$^{-7}$ mol dm$^{-3}$, [HClO$_4$] = 0.05 mol dm$^{-3}$ and I = 0.5 mol dm$^{-3}$. The rate (5.2 x 10$^{-6}$ mol dm$^{-3}$ s$^{-1}$ at 30°C) was independent of [pdp]. The rate (2.0 x 10$^{-6}$ mol dm$^{-3}$ s$^{-1}$) was likewise independent of [pdp] even in the absence of added Fe(III) and in the presence of 5 x 10$^{-6}$ mol dm$^{-3}$ Cu(II). The rate was 1.5 x 10$^{-6}$ mol dm$^{-3}$ s$^{-1}$ in the presence of Cu(II) at 25°C.

**Hexacyanoferrate(II) dependence**

Table 2 shows the results of the variation of [Fe(CN)$^{6-}_{6}$] under two different conditions and a plot of rate versus [Fe(CN)$^{6-}_{6}$] is linear passing through the origin in the two cases indicating first order dependence on [Fe(CN)$^{6-}_{6}$]. On the basis of first order in [Fe(III)] and first order in [Fe(CN)$^{6-}_{6}$], the second order rate constant was found to be 6.5 x 10$^3$ dm$^3$ mol$^{-1}$ s$^{-1}$ at 30°C for added 5.0 x 10$^{-7}$ mol dm$^{-3}$ Fe(III) i.e. total 8.0 x 10$^{-7}$ mol dm$^{-3}$

**Table 2—Dependence of initial rate on [hexacyanoferrate(II)]**

<table>
<thead>
<tr>
<th>[pdp]</th>
<th>1.0 x 10$^{-3}$ mol dm$^{-3}$; [HClO$_4$] = 0.25 mol dm$^{-3}$; I = 0.5 mol dm$^{-3}$; 30°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Fe(III)] = 5.0 x 10$^{-7}$ mol dm$^{-3}$ and no Cu(II)</td>
<td></td>
</tr>
<tr>
<td>10$^6$ [Fe(CN)$^{6-}_{6}$]/mol dm$^{-3}$</td>
<td>0.2</td>
</tr>
<tr>
<td>10$^6$ (ir)/mol dm$^{-3}$ s$^{-1}$</td>
<td>1.0</td>
</tr>
</tbody>
</table>

| [Cu(II)] = 5.0 x 10$^{-6}$ mol dm$^{-3}$ and Fe(III) only as impurity |
|------|------------------|
| 10$^6$ [Fe(CN)$^{6-}_{6}$]/mol dm$^{-3}$ | 0.2 | 0.5 | 1.0 | 2.0 | 4.0 | 6.0 | 8.0 | 10 |
| 10$^6$ (ir)/mol dm$^{-3}$ s$^{-1}$ | 0.65 | 1.3 | 2.6 | 5.2 | 10.4 | 16 | 21 | 26 |
Table 3—Initial rates (ir) of Fe(CN)$_6^{3-}$-pdp reaction in Acetate Buffers catalysed by Fe(III)

<table>
<thead>
<tr>
<th>10$^{-4}$[pdp] mol dm$^{-3}$</th>
<th>10$^{-4}$[Fe(CN)$_6^{3-}$] mol dm$^{-3}$</th>
<th>10$^{-4}$[Fe(III)]$^{3+}$ mol dm$^{-3}$</th>
<th>10$^{-7}$[Fe(III)]$^{3+}$ mol dm$^{-3}$</th>
<th>pH</th>
<th>10$^6$ (ir) mol dm$^{-3}$ s$^{-1}$</th>
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<tr>
<td>0.5</td>
<td>1.0</td>
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<td>8.0</td>
<td>4.85</td>
<td>1.2</td>
</tr>
<tr>
<td>1.0</td>
<td>1.0</td>
<td>–</td>
<td>8.0</td>
<td>4.85</td>
<td>2.3</td>
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<td>–</td>
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<td>3.9</td>
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<tr>
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<td>4.85</td>
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<td>–</td>
<td>8.0</td>
<td>4.22</td>
<td>1.9</td>
</tr>
</tbody>
</table>

†Includes [Fe(III)] present as impurity.

Fe(III) since 3.0 × 10$^{-7}$ mol dm$^{-3}$ of Fe(III) is already present in the system. A value of the rate of 2.1 × 10$^{-6}$ mol dm$^{-3}$ s$^{-1}$ under the same condition but without added Fe(III), yields a value of 7.0 × 10$^{-3}$ dm$^3$ mol$^{-1}$ s$^{-1}$ for the second order rate constant. In the presence of 5 × 10$^{-6}$ mol dm$^{-3}$ Cu(II), the second order rate constant was found to be 8.7 × 10$^{-3}$ mol$^{-1}$ dm$^3$ s$^{-1}$ employing 3 × 10$^{-7}$ mol dm$^{-3}$ for [Fe(III)].

**Hexacyanoferrate(III) dependence**

In the Cu$^{II}$/edta catalysed study, hexacyanoferrate(III) was found to inhibit the reaction and this is certainly expected from the system occurring through reaction steps (1) and (2), but in the present case hexacyanoferrate(III) is without any effect on the rate. This shows that if we were to write down reactions (1) and (2) replacing Cu$^{II}$/edta/Cu$^{II}$/edta redox cycle by Fe(III)/Fe(II) cycle, reaction (2) appears to be much faster than the back reaction of equilibrium (1). For this reason we studied the effect of Fe(CN)$_6^{3-}$ in acetate buffers. These results are given in Table 3. The inhibiting effect of Fe(CN)$_6^{3-}$ is clearly manifested. The orders in Fe(III), Fe(CN)$_6^{3-}$ and pdp were found to be one in each of them.

**Hydrogen ion dependence**

The rate decreases with the increase in [H$^+$]. A plot of rate versus [H$^+$]$^{-1}$ is linear with an intercept indicating a two term rate law as shown in Eq. (4).

$$d[Fe(CN)_6^{3-}]/dt = (k_1 + k_2/[H^+])[Fe(III)][Fe(CN)_6^{4-}]$$

... (4)

The values of $k_1$ and $k_2$ from the above plots (Fig. 2) are $5.7 \times 10^3$ mol$^{-1}$ dm$^3$ s$^{-1}$ and $3.6 \times 10^3$ mol$^{-1}$ dm$^3$ s$^{-1}$ at 30°, $6.7 \times 10^3$ mol$^{-1}$ dm$^3$ s$^{-1}$ and $23$ s$^{-1}$ at 25° and $7.0 \times 10^3$ mol$^{-1}$ dm$^3$ s$^{-1}$ and $70$ s$^{-1}$ in the presence of $5 \times 10^{-6}$ mol dm$^{-3}$ Cu(II) and at 30°. Similar [H$^+$] dependence in all the three cases confirms a two term rate law.

**Cu(II) dependence**

Copper(II) is well known for its catalytic activity in several redox reactions involving peroxodiphosphate, peroxodisulphate, hydrogen peroxide and oxygen, but the rate decreases in the present investigation. Its concentration was varied in the range (5 × 10$^{-7}$ to 1 × 10$^{-5}$) mol dm$^{-3}$ and the initial rate decreased from 8.4 × 10$^{-6}$ to 1.8 × 10$^{-6}$ mol dm$^{-3}$ s$^{-1}$. A plot of (initial rate)$^{-1}$ versus [Cu(II)] was linear with an intercept of 1.2 × 10$^6$ dm$^3$ mol$^{-1}$ s and slope of 5.2 × 10$^{11}$ dm$^6$ mol$^{-2}$ s at 30°.

**Discussion**

The species of the various reactants are determined by the hydrogen-ion dependence. Various protonated species of pdp are possible, but since the rate is independent of pdp, the species of pdp does not matter for the rate dependence. However,
the predominant species would be $H_2P_2O_7^{2-}$ on the basis of its protonation constants.$^{13}$ Fe(III) undergoes hydrolysis to yield FeOH$^2+$ species controlled by equilibrium (5)

$$K_H \frac{Fe^{3+} + H_2O}{FeOH^2+ + H^+} \quad \ldots (5)$$

The value of $K_H$ at $30^\circ$ and $I=0.5$ mol dm$^{-3}$ is $2.088 \times 10^{-3}$ mol dm$^{-3}$ on the basis of its value of $1.58 \times 10^{-3}$ mol dm$^{-3}$ at $25^\circ$ and $\Delta H=42$ kJ mol$^{-1}$. Hence Fe(III) would be about 96% in the form of Fe$^{3+}$ in 0.05 mol dm$^{-3}$ HClO$_4$. The species of hexacyanoferrate(II) are controlled by equilibrium (6) and (7).

$$K_1 \frac{Fe(CN)^{3-} + H^+}{HFe(CN)^{-}} \quad \ldots (6)$$

$$K_2 \frac{HFe(CN)^{-} + H^+}{H_2Fe(CN)^{5-}} \quad \ldots (7)$$

The values of $K_1$ and $K_2$ are reported$^{15}$ to be 526 and 83 at 25° and $I=0.5$ mol dm$^{-3}$. However, since the values at other ionic strength are reported to differ by a factor of 200, the value of $K_2$ is likely to be less than 2 and hence $HFe(CN)^{-}$ is likely to be about 90% of the total $[Fe(CN)^{-}]$.

Rate law (8) holds for the reaction in aqueous perchloric acid solutions

$$d[Fe(CN)^{3-}] / dt = k[Fe(III)][Fe(CN)^{5-}] \ldots (8)$$

However, if we take into consideration the inhibiting effect of $Fe(CN)^{5-}$ in acetate buffers, and propose general mechanism (9) and (10) on the lines of reaction studied earlier (without caring at present for actual species of the reactants), it would appear that the rate law (8) is the reduced form of (11) provided $k_3[pdp] > k_2[Fe(CN)^{5-}]$.

$$Fe(III) + Fe(CN)^{5-} -> Fe(II) + Fe(CN)^{3-} \quad \ldots (9)$$

$$Fe(II) + pdp -> [pdp] \quad \ldots (10)$$

$$d[Fe(CN)^{3-}] / dt = \frac{k_1k_3[Fe(III)][Fe(CN)^{5-}][pdp]}{k_2[Fe(CN)^{5-}] + k_3[pdp]} \ldots (11)$$

A few direct reactions with $1 \times 10^{-5}$ mol dm$^{-3}$ concentrations of Fe(II) and pdp in 0.01 mol dm$^{-3}$ HClO$_4$ at $-5^\circ$ showed that the reaction is over within the time of mixing, say 1 sec. This gives a second order rate constant $> 10^5$ mol$^{-1}$ dm$^3$ s$^{-1}$ at 30°. Since $k_1$ is $5.7 \times 10^3$ mol$^{-1}$ dm$^3$ s$^{-1}$ at 30° and $K=34$, $k_2<2 \times 10^2$ mol$^{-1}$ dm$^3$ s$^{-1}$. Thus $k_3[pdp] > k_2[Fe(CN)^{5-}]$ and it would not be possible to prove that rate law (11) holds for the reaction in acid perchlorate solutions.

In acetate buffers the mechanism appears to be more complicated owing to the complexing of Fe(III) with pdp. Nevertheless inhibition by Fe$^{3+}$ shows that equilibrium (9) in some form is operative. One natural question arises out of equilibrium (9). If this is a general mechanism for Fe$^{3+}$ oxidation in pdp reactions, is there a reductant which is oxidised by Fe$^{3+}$ through the same equilibrium? If this be so, it should be accompanied by inhibition by Fe$^{3+}$. One such reaction studied$^3$ is the reduction by $NH_3OH$ in phosphate and borate buffers, but there is no inhibition by Fe$^{3+}$. As a matter of fact in the presence of edta the rate is unexpectedly independent of Fe$^{3+}$.

However, the same reaction studied in acetate buffers (Table 4) shows that it is catalysed by Fe(II) or Fe(III) and inhibited by Fe$^{3+}$. The orders in Fe$^{3+}$, pdp and Fe(III) (impurity as well as added) are one in each. Hence in addition to equilibrium (9) being operative in this system, there are additional steps involving perhaps complex formation between Fe(II) with $NH_3OH$. These results are almost parallel to those of the oxidation of Fe$^{3+}$ by pdp in acetate buffers. Thus an oxidant which oxidises Fe$^{3+}$ slowly, but which can oxidise Fe(II) rapidly, will operate through equilibrium (9). Similarly if there is a reductant reacting slowly with Fe$^{3+}$, but quickly with Fe(III), it will work through equilibrium (9). This must happen since Fe(II) or Fe(III) is present as an impurity in the reagents or distilled water. Following mechanisms may be written for the two reactions in acetate buffers,
Table 4—Initial rates (ir) of \( \text{NH}_2\text{OH} \rightarrow \text{Fe(CN)}^\text{3-} \) reaction catalysed by Fe(III) in Acetate Buffers

\[ \text{Fe}^{\text{III}} + \text{NH}_2\text{OH} \rightarrow \text{Fe}^{\text{II}}\text{NH}_2\text{OH} \quad \text{at } t = 0.9 \text{ mol dm}^{-3}, 30^\circ \]

<table>
<thead>
<tr>
<th>( [\text{NH}_2\text{OH}] )</th>
<th>( [\text{Fe(CN)}^\text{3-}] )</th>
<th>( [\text{Fe}^{\text{III}}] )</th>
<th>( \text{pH} )</th>
<th>( \text{ir} )</th>
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\(^1\text{Includes Fe(III) present as impurity.}\)

where Fe\(^{\text{III}}\) and Fe\(^{\text{II}}\) may represent acetate complexes \(^{16}\).

**Oxidation of Fe(CN)\(^3-\) by pdp**

\[ \text{K} \]
\[ \text{Fe}^{\text{III}} + \text{pdp} \rightarrow \text{Fe}^{\text{III}}\text{pdp} \] \( \ldots (12) \)
\[ \text{K} \]
\[ \text{Fe}^{\text{III}}\text{pdp} + \text{Fe(CN)}^\text{3-} \rightarrow \text{Fe}^{\text{III}}\text{pdp} + \text{Fe(CN)}^\text{3-} \ldots (13) \]
\[ \text{Fe}^{\text{III}}\text{pdp} \rightarrow \text{products} \] \( \ldots (14) \)

If \( K \) is small and \( k_{13} \) and \( k_{14} \) are comparable, the rate law is:

\[ -d[\text{Fe(CN)}^\text{3-}] / dt = \frac{k_{17} k_{16} [\text{Fe}^{\text{III}}][\text{Fe(CN)}^\text{3-}][\text{NH}_2\text{OH}]}{k_{17} [\text{Fe(CN)}^\text{3-}] + k_{18}} \] \( \ldots (15) \)

The above rate law can account for all the results obtained for the oxidation of Fe(CN)\(^3-\) by pdp in acetate buffers.

**Reduction of Fe(CN)\(^3-\) by \text{NH}_2OH**

\[ \text{K} \]
\[ \text{Fe}^{\text{II}} + \text{NH}_2\text{OH} \rightarrow \text{Fe}^{\text{II}}\text{NH}_2\text{OH} \] \( \ldots (16) \)

Thus all the results of reduction of Fe(CN)\(^3-\) by \text{NH}_2OH in acetate buffers can be explained by rate law (19). Equilibria (13) and (17) are essentially different forms of the basic equilibrium (9). One important difference between the two mechanisms given above for acetate buffers, and the one for acid perchlorate solutions, is of complex formation of Fe(III) or Fe(II) with pdp in the former cases. In the latter case pdp is present as H\(_4\)P\(_2\)O\(_8\) and H\(_3\)P\(_2\)O\(_6\), whereas in acetate buffers it is present as H\(_2\)P\(_2\)O\(_8\) and H\(_3\)P\(_2\)O\(_6\); which will have greater tendency to complex with Fe(III) or Fe(II). There is spectropho-
It has been found that copper(II) inhibits the reaction and we also found in the spectrophotometric work that the total absorbance of the reaction mixture containing Fe(III) and Fe(CN)₆³⁻ increases in the presence of aqua Cu(II). This can happen if some of the less absorbing Fe(CN)₆³⁻ is converted into more absorbing Fe(CN)₆⁴⁻ i.e. the equilibrium is shifted to the left. In other words equilibrium concentrations of Fe(II) and Fe(CN)₆³⁻ decrease in the presence of Cu(II). Thus this effect of Cu(II) not only supports the kinetic inhibition but also establishes the fact that the redox reaction involves an equilibrium. The role of Cu(II) may be explained by the following reactions.

Fe(II) + Cu(II) → Fe(III) + Cu(I) \hspace{1cm} (24)

Cu(I) + Fe(CN)₆³⁻ → Cu(II) + Fe(CN)₆⁴⁻ \hspace{1cm} (25)

If Cu(I) is oxidised by pdp in the redox reaction, the reaction would behave normally, but it appears that Cu(I) is oxidised by Fe(CN)₆⁴⁻ rather than aq. Fe(III) or pdp. Reaction of Cu(I) with Fe(III) is fast (second order rate constant $k = 10^6$ mol⁻¹ dm³ s⁻¹ at 1.6°), but the reaction of Cu(I) with Fe₃⁺ or Fe₂⁺ is much faster (rate constant $= 10^8$ mol⁻¹ dm³ s⁻¹ at 1.6°). The reaction of Cu(I) with Fe(CN)₆⁴⁻ is likely to have a rate constant of the same order of magnitude and thus equilibrium concentrations of Fe(CN)₆⁴⁻ will be less in the presence of Cu(II).

The equilibrium constant for equilibrium (9) on the basis of oxidation potentials of Fe⁶⁺/Fe⁵⁺ and Fe(CN)₆⁴⁻/Fe(CN)₆³⁻ is $8.9 \times 10^6$ which is much larger than the experimental value. One wonders whether incomplete dissociation of KFe(CN)₆³⁻ and protonation of Fe(CN)₆⁴⁻ can modify the oxidation potentials of Fe(CN)₆⁴⁻/Fe(CN)₆³⁻ couple to such an extent that it may yield a value of 34 for $K$. However, such a large value for $K$ means that $k_1 \approx 10^7$ times $k_2$. If $k_1 = 10^3$, $k_2$ would be $\approx 10^{-4}$ on the basis of this large value. Such a low value for $k_2$ is not expected since in acetate buffers $k_2$ and $k_3$ are comparable and $k_4$ by no means can be so low. As a matter of fact Fe(II) aqua ion is not an appropriate model in conjunction with Fe(CN)₆³⁻ for the calculation of equilibrium constant from the oxidation potentials.

A comparison of the results of the oxidation of Fe(CN)₆³⁻ (this work and the previous one) and the reduction of Fe(CN)₆⁴⁻ seems to be interesting so far the effect of the two metal ion impurities of Fe(III) and Cu(II) is concerned. Oxidation of Fe(CN)₆³⁻ at $pH = 2$ was catalysed by aqua Fe(III) and Cu(II)edta, Fe(III)edta had no effect and the reaction was inhibited by aqua Cu(II). Reduction of Fe(CN)₆⁴⁻ at $pH = 6.9$ and 9.2 was inhibited by aqua Fe(III), unaf-
fected by Cu(II)edta and catalysed by Fe(III)edta and aqua Cu(II).

The aquo species of Fe(III) and Cu(II) have just the opposite effects in the two systems and hence both the reactions appear to occur by similar mechanisms viz., equilibrium (9). The copper(II) inhibition has already been explained. The inhibition by Fe(III) is explained through equilibrium (9) which becomes favourable towards the right thus increasing Fe(III) and retarding the rate.

The two rate constants of the rate law (20) can be calculated by Marcus cross relation given by (26)

$$k_{12} = (k_{11}k_{22}K_{12})^{1/2}$$

where $k_{11}$ and $k_{22}$ are the isotopic exchange rate constants for Fe$^3+$/Fe$^2+$ and Fe(CN)$^{5-}$/Fe(CN)$^{6-}$ couple respectively, $k_{12}$ is the equilibrium constant for the redox reaction Fe(III) + Fe(CN)$^{6-}$. The value of $k_{22}$ is $2.45 \times 10^4$ at $30^\circ$ on the basis of its value of 1.9 $\times 10^4$ mol$^{-1}$ dm$^3$ s$^{-1}$ at $25^\circ$ and energy of activation of 38 kJ mol$^{-1}$. The value for HFe(CN)$^{6-}$/HFe(CN)$^{5-}$ couple is not known but it is likely to be larger than for Fe(CN)$^{6-}$/Fe(CN)$^{5-}$ couple since $H^+$ catalyses the isotopic exchange rate.

The value of $k_{11}$ at $30^\circ$ is 4.76 mol$^{-1}$ dm$^3$ s$^{-1}$ using the value of 0.87 dm$^3$ mol$^{-1}$ s$^{-1}$ at $0^\circ$ and $\Delta H = 39$ kJ mol$^{-1}$. Using these values of $k_{11}$ and $k_{22}$, and $K_{12} = 34$, $k_{12}$ was found to be $5.2 \times 10^3$ mol$^{-1}$ s$^{-1}$ at $30^\circ$. The experimental value was found to be $5.7 \times 10^3$ dm$^3$ mol$^{-1}$ s$^{-1}$. For the $H^+$ dependent path $k_{12}$ was found to be $4.7 \times 10^4$ dm$^3$ mol$^{-1}$ s$^{-1}$ at $30^\circ$ on the basis of $k_{11}$ (FeOH$^+/Fe^{2+}$) equal to $3.5 \times 10^3$ dm$^3$ mol$^{-1}$ s$^{-1}$ (calculated from the value of 1 $\times 10^3$ dm$^3$ mol$^{-1}$ s$^{-1}$ at $0^\circ$ and $\Delta H = 29$ kJ mol$^{-1}$) and the same value of $k_{22}$ and $K_{12}$. The experimental value is $36$ s$^{-1}$. The agreement is not satisfactory. For the alternative path (Fe$^{3+}$/Fe(CN)$^{6-}$) the calculated value of $k_{12}$ is $520$ mol$^{-1}$ dm$^3$ s$^{-1}$ which is in better agreement of the experimental value of $36$ s$^{-1}$. Hence the latter appears to be the $H^+$ dependent path. The fact that the exchange rates of the system were not reproducible in acid solutions and in absence of edta, indicates the involvement of an equilibrium like (9) in the Fe(CN)$^{6-}$/Fe(CN)$^{5-}$ systems.

The fact that the blue precipitate obtained by mixing Fe$^{3+}$ and Fe(CN)$^{6-}$ or Fe$^{2+}$ and Fe(CN)$^{5-}$ is the same, i.e., Fe$^{III}_{(aq)}[Fe^{III}(CN)_6]xH_2O$, also indicates the existence of an equilibrium like (9). It is basically the reaction between Fe$^{3+}$ and Fe(CN)$^{6-}$, but Fe$^{2+}$ and Fe(CN)$^{5-}$ also give the same precipitate by first forming Fe$^{3+}$ and Fe(CN)$^{6-}$ through equilibrium (9).

References

6. Ref. 5, p. 212.
22. Ref. 20, p. 208.