Kinetics and Mechanism of Oxidations by Peroxodiphosphate Ions. Part 7.† Role of Trace Metal Ions, and Catalysis by Ethylenediaminetetra-acetatocopper(II) in the Oxidation of Hexacyanoferrate(II) in Acid Perchlorate Media

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Oxidation of $[Fe(CN)]_6{}^{4-}$ by peroxodiphosphate [equation (i)] is influenced by trace iron(II) and copper(II) ions

$$2[Fe(CN)_6]^{4-} + H_2P_2O_8{}^{2-} \longrightarrow 2[Fe(CN)_6]^{3-} + 2HPO_4{}^{2-} \qquad \text{(i)}$$

present in the distilled water and the reagents used. A detailed study has shown that Fe^{2+}(aq), Fe^{3+}(aq), and $[Cu(edta)]^{2-}$ catalyse the reaction, $[Fe(edta)]^{2-}$ and $[Fe(edta)]^{-}$ (edta = ethylenediaminetetra-acetate) are not reactive, and Cu^{2+}(aq) inhibits the reaction. The increase in hexacyanoferrate(III) concentration has been followed colorimetrically and rate of reaction in the presence of edta and added Cu^{II} is given by (ii), where $[Fe^{II}]$,

$$\frac{d[Fe(CN)_6{}^{3-}]}{dt} = \frac{k_1'[Cu(edta)^{2-}][Fe^{II}][\text{peroxodiphosphate}]}{k_2'[Fe^{III}] + k_3'[\text{peroxodiphosphate}]} \qquad \text{(ii)}$$

$[Fe^{III}]$, and [peroxodiphosphate] are the total concentrations of the iron(II), iron(III), and peroxodiphosphate species respectively. The hydrogen-ion dependent values of k_1'/k_2' and k_3'/k'_2 are 5.9 ± 1.1 and $(1.09 \pm 0.24) \times 10^{-1}$ respectively at 35 °C and $[H^+] = 0.05$ mol dm^{-3}. The reactive species and the mechanism are as in equations (iii) and (iv).

$$[Cu(edta)]^{2-} + [HFe(CN)_6]^{3-} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} [Cu(edta)]^{3-} + [HFe(CN)_6]^{2-} \qquad \text{(iii)}$$

$$[Cu(edta)]^{3-} + H_4P_2O_8 \xrightarrow{k_3} [Cu(edta)]^{2-} + \text{products} \qquad \text{(iv)}$$

THE slow step of the hydrolysis of peroxodiphosphate to peroxomonophosphate is a general feature of redox reactions[1-4] involving peroxodiphosphate. However, there are two exceptions. The oxidation of iodide[5,6] occurs in two or three parallel paths involving peroxodiphosphate species in addition to hydrolytic species. The main exception is found in the oxidations of iron(II) complexes[7,8] in neutral media where under certain conditions the rate is independent of the oxidant. The essential feature of these oxidations is the dissociation of the tris complexes. The rate constants for the redox reaction and for the dissociation of the tris-(1,10-phenanthroline), -(2,2′-bipyridyl), and -(2,2′:6,2″-terpyridyl) complexes are almost the same (*ca.* 10^{-4} s^{-1} at 25 °C), and the Scheme shows the mechanism which has been suggested (rating the phen complex as an example).

$$[Fe(phen)_3]^{2+} \rightleftharpoons [Fe(phen)_2]^{2+} + phen$$
$$[Fe(phen)_2]^{2+} + P_2O_8{}^{4-} \longrightarrow \text{products}$$

SCHEME

Our interest in the oxidation of hexacyanoferrate(II) lay in whether this oxidation occurred by a simple bimolecular mechanism as in the case of peroxodisulphate[9,10] or by a mechanism somewhat similar to that in the Scheme. Copper(II) catalysis of this reaction was not originally a subject of study, but it became so subsequently when traces of Cu^{II} present in the reagents and distilled water were found to influence the rate of reaction.

A paper[11] on the oxidation of hexacyanoferrate(II) with peroxodiphosphate at pH 8 came to our notice after completion of the present work. In that reaction a peroxodiphosphate-substituted inner-sphere complex of hexacyanoferrate(II) is considered to decompose in the rate-determining step. The rate is retarded in the presence of cyanide, and many features of the study remain unexplained. The present work, carried out in an acidic medium, describes the role of hydrogen ion, the effect of hexacyanoferrate(III) on the rate, and the mechanism by which trace metal-ion catalysis operates in such systems.

EXPERIMENTAL

Materials.—Tetrapotassium peroxodiphosphate, $K_4[P_2O_8]$, was a gift from FMC Corporation, U.S.A. Its solutions were prepared by direct weighing and standardized cerimetrically[7] and iodometrically.[12] Potassium hexacyanoferrate(II) was B.D.H. AnalaR quality and its solutions were always freshly prepared and standardized cerimetrically.[13] The disodium salt of ethylenediaminetetra-acetic acid, $Na_2[H_2edta]$, was E. Merck quality. 70% Perchloric acid was AnalaR (Riedel). Lithium perchlorate was prepared by neutralizing perchloric acid with lithium carbonate to pH 6.7. Copper(II) sulphate and all other chemicals were B.D.H. AnalaR quality. All solutions were prepared in doubly distilled water, the second distillation being from neutral potassium permanganate. All glass vessels were cleaned with sodium carbonate and steamed before use.

Kinetic Procedure.—Requisite quantities of copper(II) sulphate, $Na_2[H_2edta]$, perchloric acid, lithium perchlorate or any other salt, and hexacyanoferrate(II) were thermostatted in a reaction vessel in a water-bath at 35 ± 0.1 °C unless stated otherwise. Tetrapotassium peroxodiphosphate, separately equilibrated, was added to the reaction vessel to initiate the reaction. There was no reaction prior to the

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† Part 6, L. M. Bharadwaj, D. N. Shama, and Y. K. Gupta, *Inorg. Chem.*, 1978, **17**, 2469.

addition of peroxodiphosphate. The total volume of the reaction mixture was 100 cm^3. Aliquot portions (5 cm^3) were removed after suitable time intervals, added to 1.0 mol dm^{-3} Na[OH] (5 cm^3), and analyzed at 420 nm on a Spectronic 20 colorimeter. The absorption coefficient of hexacyanoferrate(III) is 1 020 ± 10 dm^3 mol^{-1} cm^{-1} at 420 nm; potassium hexacyanoferrate(II) is transparent at this wavelength. Reaction mixtures were flushed with purified nitrogen gas throughout the run.

No precipitate of $Cu_2[Fe(CN)_6]$ was formed in the system under the conditions employed. Since the rate is inhibited by $[Fe(CN)_6]^{3-}$, most of the reactions have been studied in the presence of added $[Fe(CN)_6]^{3-}$. Owing to the complexity of the system, the data were treated on the basis of initial rates determined by the plane-mirror method.[14] Integrated first-order plots were made only in those cases where large concentrations of $[Fe(CN)_6]^{4-}$ and $[Fe(CN)_6]^{3-}$ were employed and the results were in agreement with those obtained from initial rates. A preliminary study indicated that no reaction occurred in 1.0 mol dm^{-3} Na[OH]. This fact was made use of in quenching the reaction.

TABLE 1

Stoicheiometry of the reaction between hexacyanoferrate(II) and peroxodiphosphate

$10^3[Fe(CN)_6{}^{4-}]$ (taken)	$10^3[P_2O_8{}^{4-}]$ (taken)	$10^3[Fe(CN)_6{}^{3-}]$ (found)	$10^3[Fe(CN)_6{}^{4-}]$ (remaining)	$10^3[P_2O_8{}^{4-}]$ (remaining)	$\frac{[Fe(CN)_6{}^{4-}]_{reacted}}{[P_2O_8{}^{4-}]_{reacted}}$
2.00	0.435	0.88	1.10		2.07
2.00	0.875	1.78	0.20		2.05
4.00	1.305	2.60	1.35		2.03
1.00	1.750	1.00		1.240	1.96
1.00	0.875	1.00		0.365	1.96
2.00	1.750	2.00		0.740	1.98

All concentrations are in mol dm^{-3}; [Cu^{II}] = 7.5 × 10^{-6}, [HClO$_4$] = 0.05, and [edta] = 0.01 mol dm^{-3}.

Trace impurities of copper(II) and iron(II) or iron(III) in the distilled water and in the reagents employed greatly catalyse the rates of reactions [15-17] involving hexacyanoferrate(II) and/or hexacyanoferrate(III). Trace amounts of calcium(II) and barium(II) also present in distilled water influence the isotopic exchange [18] rate between hexacyanoferrate-(II) and -(III). Trace amounts of copper(II) ions also have a catalytic effect on oxidations [19,20] by peroxodiphosphate. One consequence of this trace metal-ion catalysis is that the results are not reproducible and a similar trend was found in the present case. Ethylenediaminetetra-acetate [21] was therefore employed to mask the effect of these ions by complexing them. Although the reproducibility improved significantly, the results were still not satisfactory. However, by using the same solutions of all the reactants, the reproducibility improved to ±15%.

Perchloric acid equal to twice the concentrations of peroxodiphosphate and $Na_2[H_2edta]$ was added to convert them to $H_2P_2O_8{}^{2-}$ and edta^{4-} respectively. The concentration of perchloric acid shown in the Tables is that present after making these adjustments, wherever necessary.

RESULTS AND DISCUSSION

Stoicheiometry.—Reactions were examined after complete reaction by analysis for $[Fe(CN)_6]^{3-}$ formed and either residual $[Fe(CN)_6]^{4-}$ or peroxodiphosphate. For the conditions shown in Table 1, each mol of peroxodiphosphate required 2.01 ± 0.04 mol of $[Fe(CN)_6]^{4-}$.

Role of edta, and Aquo- and edta Complexes of Cu^{II} *and* Fe^{II}.—Since edta had to be employed to complex trace metal ions and improve reproducibility, it was necessary to carry out systematic studies with edta. Typical results with increasing amounts of edta without and with added Cu^{II} are shown in Figure 1. The rate of reaction decreases with increasing [edta] and then attains a limiting value. There is a larger rate in the presence of added Cu^{II}. This indicates that [Cu(edta)]$^{2-}$ is reactive. A few experiments were carried out with Cu^{II}, Fe^{II}, and Fe^{III} with and without edta and the results are given in Table 2. The results when no metal ions were added are not given since they were not reproducible.

It is obvious that Cu^{2+}(aq) is not a catalyst since it retards the rate. It is also obvious that Fe^{2+}(aq) has great catalytic activity, but the edta complex of Fe^{II} has none, and that the decrease in the rate of Figure 1 can be ascribed to the complexing of reactive Fe^{2+} (aq). Thus Fe^{2+} (aq) and [Cu(edta)]$^{2-}$ seem to be reactive. This in a way is supported by the observations made on the trace metal-ion catalyzed reduction [17] of $[Fe(CN)_6]^{3-}$ by NH$_2$OH wherein [Fe(edta)]$^-$ and Cu^{2+}

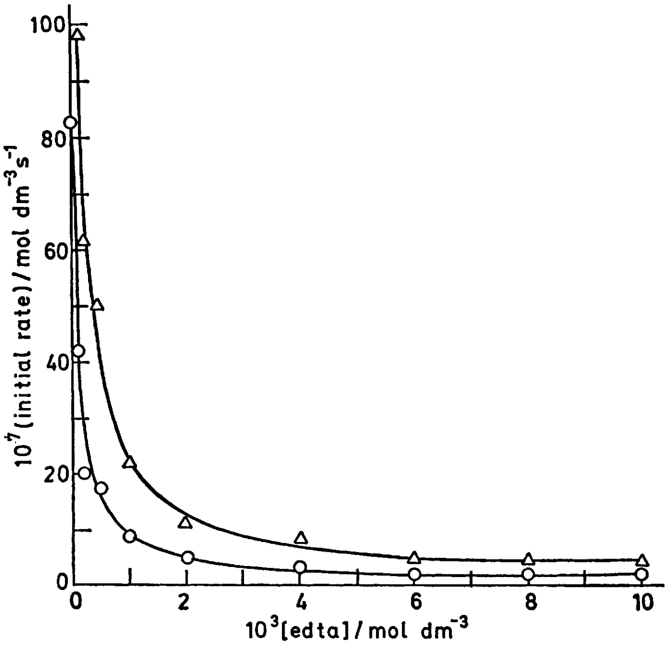

FIGURE 1 Effect of edta on the initial rate of reaction in the presence (△) and absence (○) of 5.0 × 10^{-7} mol dm^{-3} Cu^{II}. [peroxodiphosphate] = 1.0 × 10^{-3}, $[Fe(CN)_6{}^{4-}]$ = 1.0 × 10^{-2}, [HClO$_4$] = 0.05 mol dm^{-3}, 35 °C

were found to be reactive and Fe^{2+}(aq) was found to inhibit[21] the reaction.

Table 3 shows the effect of variation of copper(II) concentration on the rate of reaction in the presence of different concentrations of edta. It is difficult to report any regularity with regard to either [Cu^{II}] variation at fixed [edta] or variation of [edta] at fixed [Cu^{II}] in view of the different opposite behaviours of iron(II) and copper(II). However, two things are obvious. At high concentrations of edta (0.01 and 0.02 mol dm^{-3}), the initial rates are almost similar showing complete complexing of copper(II) added, and iron(II) present as impurity. Further, at low concentrations of edta (1×10^{-4} mol dm^{-3}), complexing may be complete for lower concentrations of copper(II), but a large concentration of free Cu^{2+}(aq) may exist at high concentrations of Cu^{II}. Thus for 1×10^{-4} mol dm^{-3} edta, variation of [Cu^{II}] first yields an increase in rate and then a decrease. Although the complex-formation constant[22] for [Cu(edta)]$^{2-}$ is large, the concentration of complexing species of edta (probably tri- or di-protonated) is small in the acid medium since pK_1 and pK_2 of edta are reported[23] to be small.

TABLE 2

Effect of Fe^{II} and Fe^{III} on the initial rates (v_0) of the $[Fe(CN)_6]^{4-}$–$P_2O_8^{4-}$ reaction in the absence and presence of edta at 35 °C

		[edta] = 0.0			
10^8[Fe^{II}]/mol dm^{-3}		0.1	1.0	10.0	100.0
10^6 v_0/mol dm^{-3} s^{-1}			11.0	13.0	23.6
		[edta] = 2×10^{-3} mol dm^{-3}			
10^8[Fe^{II}]/mol dm^{-3}	0.0	0.1	1.0	10.0	100.0
10^6 v_0/mol dm^{-3} s^{-1}	1.9	1.9	1.7	1.8	1.7
		[edta] = 0.0			
10^8 [Fe^{III}]/mol dm^{-3}		5.8	10.0	20.0	100.0
10^6 v_0/mol dm^{-3} s^{-1}		7.3	9.0	11.6	15.0
		[edta] = 1×10^{-2} mol dm^{-3}			
10^8 [Fe^{III}]/mol dm^{-3}	0.0	5.8	10.0	20.0	100.0
10^6 v_0/mol dm^{-3} s^{-1}	1.0	0.96	0.93	1.06	1.03
		[edta] = 0.0			
10^6 [Cu^{II}]/mol dm^{-3}		1.0	10.0	20.0	60.0
10^6 v_0/mol dm^{-3} s^{-1}	18.3	8.0	4.7	4.7	1.25

[peroxodiphosphate] = 1×10^{-3}, [$Fe(CN)_6^{4-}$] = 1×10^{-2}, and [$HClO_4$] = 0.05 mol dm^{-3}.

A plot of initial rate *versus* [Cu^{II}] for 1×10^{-2} and 2×10^{-2} mol dm^{-3} edta is linear with an intercept which corresponds to 7.5×10^{-6} mol dm^{-3} copper(II) impurity in the reacting system.[24] The rate of reaction appears to have a first-order dependence on the concentration of [Cu(edta)]$^{2-}$.

Hexacyanoferrate(II) *Dependence*.—The concentration of hexacyanoferrate(II) was varied from 2.5×10^{-4} to 2×10^{-2} mol dm^{-3} and a plot of rate *versus* [$Fe(CN)_6^{4-}$] yielded a straight line passing through the origin and with a slope of $(1.09 \pm 0.05) \times 10^{-4}$ s^{-1}, indicating a first-order dependence on hexacyanoferrate(II) concentration.

Peroxodiphosphate Dependence.—The concentration of peroxodiphosphate was varied in the range 2.5×10^{-4}—3.0×10^{-3} mol dm^{-3} at 35 and 45 °C at fixed concentrations of other reactants and different concentrations of added hexacyanoferrate(III). The results are shown in Table 4. A plot of rate *versus* [peroxodiphosphate] is a curve tending to a limiting value at large concentrations of peroxodiphosphate. Reciprocal plots of rate and [peroxodiphosphate] yield straight lines with the same intercept but different slopes. The ratio of intercept to slope, which is equal to k_3'/k_2' of equations (iii) and (iv) in the Summary, was found to be 0.085 ± 0.006 at 35 °C and [H^+] = 0.05 mol dm^{-3}; from the

TABLE 3

Effect of Cu^{II} on the initial rate (v_0) of the $[Fe(CN)_6]^{4-}$–$P_2O_8^{4-}$ reaction in the presence of different concentrations of edta at 35 °C

	[edta]/mol dm^{-3}				
10^6[Cu^{II}]/mol dm^{-3}	0.0	1.0×10^{-4}	2.0×10^{-4}	1.0×10^{-2}	2.0×10^{-2}
	10^6 v_0/mol dm^{-3} s^{-1}				
0.0		11.6		0.62	0.63
1.0	18.3	12.5	2.7		
2.5	16.6	13.6	4.7	0.75	1.05
5.0	10.0	14.6	5.3	1.2	1.25
10.0	8.0	12.6	7.0	1.65	2.0
20.0	4.7	10.8	8.7	2.25	2.5
30.0		9.2		3.2	3.5
40.0	1.75	8.7	13.0	4.5	4.8
60.0	1.25				

[peroxodiphosphate] = 1×10^{-3}, [$Fe(CN)_6^{4-}$] = 1×10^{-2}, and [$HClO_4$] = 0.05 mol dm^{-3}.

TABLE 4

Peroxodiphosphate dependence in the $[Fe(CN)_6]^{4-}$–$P_2O_8^{4-}$ reaction at 35 °C

	10^4[$Fe(CN)_6^{3-}$]/mol dm^{-3}					
	2.0	3.0	4.0	12.0	2.0 *	12.0 *
10^4[peroxodiphosphate]/mol dm^{-3}	10^7 v_0/mol dm^{-3} s^{-1}					
2.50	4.3	3.33	2.7	1.5 (5.8)	5.6	2.1 (8.4)
5.00	8.0	6.3	5.2	2.7 (5.4)	10.5	4.4 (8.8)
10.00	14.6	11.5	10.0	5.0 (5.1)	20.0	8.8 (8.4)
12.50	17.7	13.2	11.5	6.3 (5.2)	21.5	10.5 (8.6)
15.00	19.3	19.3	15.5	7.6 (5.0)	24.0	13.0 (8.7)
17.50	20.6	17.5	14.5	8.6 (4.9)	31.5	16.0 (9.1)
20.00	22.5	19.0	16.5	10.2 (5.1)	33.5	17.0 (8.6)
30.00	28.3					

[$Fe(CN)_6^{4-}$] = 1×10^{-2}, [Cu^{II}] = 1×10^{-5}, [edta] = 1×10^{-2}, and [$HClO_4$] = 0.05 mol dm^{-3}. Figures in parentheses are the pseudo-first-order rate constants ($\times 10^4$) obtained from plots of log [peroxodiphosphate] *versus* time.

* At 45 °C.

TABLE 5

Hexacyanoferrate(III) dependence in the $[Fe(CN)_6]^{4-}$–$P_2O_8^{4-}$ reaction

10^4 $[Fe(CN)_6^{3-}]$/mol dm^{-3}	10^3[peroxodiphosphate]/mol dm^{-3}		
	1.0	2.0	1.0 *
	10^7 v_0/mol dm^{-3} s^{-1}		
2.0	18	25	24
3.0	15	21	20
4.0	12.5	20	17
6.0	9.4	15.5	14
8.0		13	12
10.0	6.0	11	10
12.0	5.0	9.6	9

$[Fe(CN)_6^{4-}] = 1 \times 10^{-2}$, $[Cu^{II}] = 1 \times 10^{-5}$, [edta] $= 1 \times 10^{-2}$, and $[HClO_4] = 0.05$ mol dm^{-3}.

* At 45 °C.

slope k_1'/k_2' was found to be 4.25 ± 0.30. In the presence of 1.2×10^{-3} mol dm^{-3} $[Fe(CN)_6]^{3-}$ the plots of rate *versus* [peroxodiphosphate] yield straight lines passing through the origin, indicating a first-order dependence on the concentration of peroxodiphosphate. Thus the dependence on peroxodiphosphate is complex and a function of the hexacyanoferrate(III) added. The value of k_1'/k_2' from such a plot was found to be 6.12 ± 0.36 at 35 °C and $[H^+] = 0.05$ mol dm^{-3}.

Effect of Hexacyanoferrate(III).—One of the products of reaction is hexacyanoferrate(III) and hence the reactions were studied in its presence to see whether the rate-determining step is preceded by an equilibrium step. The concentration of hexacyanoferrate(III) was varied in the range 2×10^{-4}—1.2×10^{-3} mol dm^{-3} at two temperatures and two concentrations of peroxodiphosphate and at fixed concentrations of other reactants. The results are given in Table 5. Plots of reciprocal initial rates *versus* $[Fe(CN)_6^{3-}]$ yielded straight lines with an intercept. The values of k_3'/k_2' and k_1'/k_2' from such plots were found to be 0.133 ± 0.041 and 6.95 ± 0.30 respectively at 35 °C and $[H^+] = 0.05$ mol dm^{-3}. Thus the internal consistency of the results from the two plots is satisfactory.

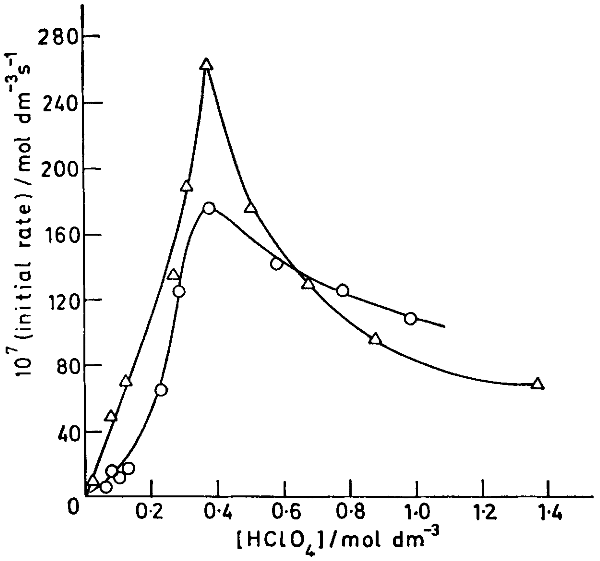

FIGURE 2 Hydrogen-ion dependence of the reaction between peroxodiphosphate and $[Fe(CN)_6]^{4-}$ in the presence of a small concentration of $[Fe(CN)_6]^{3-}$ (2×10^{-4} mol dm^{-3}) at 35 °C and $I = 1.5$ mol dm^{-3}. [peroxodiphosphate] $= 1 \times 10^{-3}$ (○) or 5×10^{-2} (△), $[Fe(CN)_6^{4-}]$ = [edta] $= 1 \times 10^{-2}$, and $[Cu^{II}] = 10^{-5}$ mol dm^{-3}

Hydrogen-ion Dependence.—The hydrogen-ion concentration was varied with $HClO_4$ in the range 0.05—1.5 mol dm^{-3} at constant $I = 1.5$ mol dm^{-3} adjusted with lithium perchlorate and at fixed concentrations of other reactants. These results are given in Figures 2 and 3. Two characteristics are obvious from the hydrogen-ion dependence: (1) for lower concentrations of added $[Fe(CN)_6]^{3-}$ the rate passes through a maximum; and (2) for larger concentrations of $[Fe(CN)_6]^{3-}$ the rate attains a limiting value with increasing hydrogen-ion concentration.

Oxidations of Hexacyanoferrate(II) *with Peroxodisulphate and Hydrogen Peroxide*.—Since the structures of peroxodisulphate and hydrogen peroxide are similar to that of peroxodiphosphate, a comparative study of $[Cu(edta)]^{2-}$-catalyzed oxidations of hexacyanoferrate(II) with these oxidants was undertaken. These oxidations seem to be straightforward with orders of one with respect to the concentrations of Fe^{II}, oxidant, and $[Cu(edta)]^{2-}$. They have inverse first-order dependences on hexacyanoferrate(III) concentration.

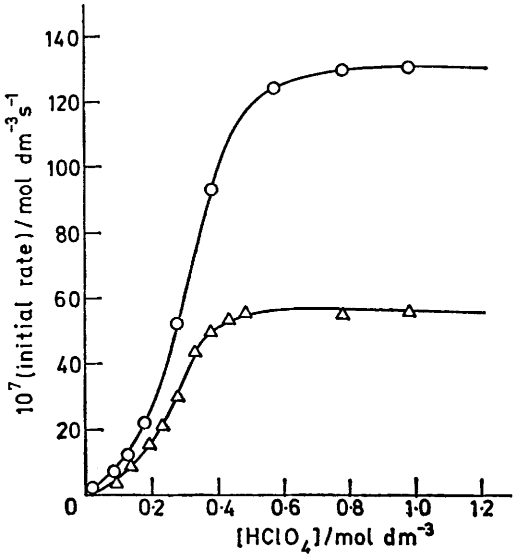

FIGURE 3 Hydrogen-ion dependence as in Figure 2 but in the presence of a large concentration of $[Fe(CN)_6]^{3-}$ [1.0×10^{-3} (○) or 2.0×10^{-3} mol dm^{-3} (△)]. Other details as in Figure 1, except for [peroxodiphosphate] $= 1 \times 10^{-3}$ mol dm^{-3}

Mechanism.—In the present work the hydrogen-ion concentration is controlled by equilibria (1)—(4).

$$H_2P_2O_8^{2-} + H^+ \overset{K_1}{\rightleftharpoons} H_3P_2O_8^- \qquad (1)$$

$$H_3P_2O_8^- + H^+ \overset{K_2}{\rightleftharpoons} H_4P_2O_8 \qquad (2)$$

Crutchfield and Edwards[25] have reported 3.3 and 0.5 dm^3 mol^{-1} for K_1 and K_2, while Venturini *et al.*[26] and

Gupta and co-workers [2] have shown that these values cannot be greater than 0.025 and 0.012 5 dm^3 mol^{-1} respectively. Thus $H_2P_2O_8^{2-}$ would exist predominantly in such systems. K_3 and K_4 are reported [27,28] to be *ca.* 2×10^4 and 2×10^2 dm^3 mol^{-1} at 25 °C and $I = 0$. The enthalpy changes for the protonation equilibria (3)

$$[Fe(CN)_6]^{4-} + H^+ \overset{K_3}{\rightleftharpoons} [HFe(CN)_6]^{3-} \qquad (3)$$

$$[HFe(CN)_6]^{3-} + H^+ \overset{K_4}{\rightleftharpoons} [H_2Fe(CN)_6]^{2-} \qquad (4)$$

and (4) are approximately zero and hence K_3 and K_4 would vary little with temperature, but these decrease considerably with the increase in ionic strength. The values [29] at 30 °C and $I = 0.025$ mol dm^{-3} are 1.5×10^3 and 40 dm^3 mol^{-1} respectively. Thus all the three species $[Fe(CN)_6]^{4-}$, $[HFe(CN)_6]^{3-}$, and $[H_2Fe(CN)_6]^{2-}$ would exist in comparable concentrations in the acidic

$$[Cu(edta)]^{2-} + [HFe(CN)_6]^{3-} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} [Cu(edta)]^{3-} + [HFe(CN)_6]^{2-} \qquad (5)$$

$$[Cu(edta)]^{3-} + H_4P_2O_8 \xrightarrow{k_3} \text{products} \qquad (6)$$

solutions employed. The ion $[Fe(CN)_6]^{3-}$ can also be protonated but the value of the protonation constant, K_5, is small [22] and the predominant form of Fe^{III} would be $[Fe(CN)_6]^{3-}$.

On the basis of the results obtained, the mechanism in equations (5) and (6) may be suggested. Applying the steady-state treatment to $[Cu(edta)]^{3-}$, rate law (7) is obtained. Here $[Fe^{II}]$, $[Fe^{III}]$, and [peroxodiphosphate] are the analytical concentrations of iron(II), iron(III), and peroxodiphosphate respectively. Thus k_1', k_2', and k_3' values of equation (ii) (see Summary) can easily be identified from the above equation at constant [H$^+$].

$$d[Fe^{III}]/dt = \frac{k_1k_3K_2K_3[Cu(edta)^{2-}][Fe^{II}][\text{peroxodiphosphate}][H^+]^2}{(1 + K_3[H^+] + K_3K_4[H^+]^2)(k_2K_5[Fe^{III}] + k_3K_1K_2[\text{peroxodiphosphate}][H^+])} \qquad (7)$$

There are two conditions under which the hydrogen-ion dependence may be simplified: (*i*) when $k_2K_5[Fe^{III}] \gg k_3K_1K_2[\text{peroxodiphosphate}][H^+]$ and (*ii*) when $k_3K_1K_2[\text{peroxodiphosphate}][H^+] \gg k_2K_5[Fe^{III}]$. The expected curves of the plots under these two conditions are given in Figures 2 and 3. The reactions in highly acidic media conforming to a simpler rate law could not be studied since they are too fast for conventional methods of analysis. By making plots of suitable functions of rate and [H$^+$] at high and low [H$^+$] one can make rough estimates of K_3 and K_4, which were found to be 8.2 and 2.8 dm^3 mol^{-1} at $I = 1.5$ mol dm^{-3}. With these values, and those of 0.025 and 0.012 5 dm^3 mol^{-1} for K_1 and K_2, k_1 and k_1k_3/k_2 were calculated from several possible plots of hydrogen-ion dependence as $(2.4 \pm 1.1) \times 10^2$ and $(11.4 \pm 2.2) \times 10^5$ dm^3 mol^{-1} s^{-1} respectively.

If rates of reaction at different [H$^+$] are calculated on the basis of rate law (7) and compared with the values given in Figures 2 and 3, a maximum rate is found in the [H$^+$] range 0.35—0.40 mol dm^{-3} when the concentration of hexacyanoferrate(III) added is small. A limiting rate is found when the concentration of hexacyanoferrate(III) added is large. The calculated and observed rates are in good qualitative agreement.

There is indirect evidence for the existence of equilibrium (5). Thus if ascorbic acid is added to a mixture of $[Cu(edta)]^{2-}$ and $[Fe(CN)_6]^{4-}$ in acid solution the chocolate brown colour disappears. The reaction [30] of ascorbic acid with hexacyanoferrate(III) is fast and equilibrium (5) is shifted to the right. There was no reaction [31] between $[Cu(edta)]^{2-}$ and ascorbic acid in the acidic medium employed. Secondly, if acrylamide is added to a mixture of $[Cu(edta)]^{2-}$ and hexacyanoferrate(II) in acidic solution the chocolate brown colour disappears, indicating a shift of equilibrium (5) and the formation of a complex of Cu^I with acrylamide.

On the basis of oxidation potentials the equilibrium constant for reaction (8) is *ca.* 6×10^{-11} at 25 °C. Since the oxidation potential for the $[Fe(CN)_6]^{4-}$–$[Fe(CN)_6]^{3-}$ couple is less negative than that of Fe^{2+}(aq)–Fe^{3+}(aq), and the oxidation potential of the $[Cu(edta)]^{3-}$–$[Cu(edta)]^{2-}$ couple is likely to be more negative than that of Cu^+(aq)–Cu^{2+}(aq), the equilibrium constant for reaction (5) is likely to be larger than 6×10^{-11} and hence is more favourable towards the right. One can thus explain the $[Cu(edta)]^{2-}$ catalysis. However, the retardation by Cu^{2+}(aq) in the absence of edta in the present reaction is surprising, although a similar behaviour is reported in the oxidation [32] of uranium(IV) by H_2O_2.

$$Fe^{2+} + Cu^{2+} \rightleftharpoons Fe^{3+} + Cu^I \qquad (8)$$

In the oxidation of hydroxylamine [21] with hexacyanoferrate(III), Cu^{2+}(aq) and not the edta complex is the catalyst. Incidently, this is a reduction of Fe^{III}, and the behaviour of Fe^{2+}(aq) in the two reactions is also opposite. It may be mentioned that perhaps all hexacyanoferrate(II) oxidations are catalyzed by $[Cu(edta)]^{2-}$ and not by Cu^{2+}(aq), and that catalysis observed in the absence of edta is due to Fe^{2+}(aq) or Fe^{3+}(aq).

Some more indirect evidence for equilibrium (5) may be obtained from the following examples. Bridgart and Wilson [16] suggest an equilibrium of this type in the oxidation of thiols by hexacyanoferrate(III) with an equilibrium constant of *ca.* 1×10^{-15} at 25 °C. A similar equilibrium has been reported [33] in the oxidation of hexacyanoferrate(II) by $[Co(edta)]^-$ with an equilibrium constant of 4.66×10^{-2} at 25 °C [equation (9)]. They

$$[Co(edta)]^- + [Fe(CN)_6]^{4-} \rightleftharpoons [Co(edta)]^{2-} + [Fe(CN)_6]^{3-} \qquad (9)$$

and several other workers [34] studied the back reaction of equilibrium (9). Such a study of back and forward reactions of equilibrium (5) does not seem to have been made so far. However, Espenson *et al.*[35] studied the back reaction of equilibrium (8) and found the rate constant to be 1.2×10^5 dm^3 mol^{-1} s^{-1} at 25 °C and $I = 1.0$ mol dm^{-3}.

It is interesting to note that copper(II) also has catalytic activity in the oxidations [of hexacyanoferrate(II)] by H_2O_2 or $S_2O_8^{2-}$. In all probability the catalysis occurs *via* equilibrium (5) and additional support to this mechanism is the retardation by hexacyanoferrate(III).

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