Metal-ion Catalysis in Some Reactions of Hexacyanoferrate(III). Part III.[1] The Oxidation of Hydroxylamine

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The oxidation of hydroxylamine by hexacyanoferrate(III) is efficiently catalysed by (edta)iron(III) and by aquocopper(II). The pentacyanoaquoferrates and other secondary reaction products are not significant catalysts.

During a study[2] of the oxidation of hydroxylamine and some of its derivatives, Gutch and Waters found that the oxidation of hydroxylamine by hexacyanoferrate(III) [hereafter referred to as cyanoferrate(III)] formed a relatively stable radical species, but only in the presence of carbonate. They thought it to be $^{\bullet}O{-}NH{-}CO_2^-$, derived from *N*-hydroxycarbamate, $HO{-}NH{-}CO_2^-$. This surprising observation led us to make the kinetic study of the reaction now reported. We find that the reactions are subject to efficient catalysis by aquocopper(II), and by the edta complexes of iron. There are close similarities between the present system and the oxidation of cysteine and related thiols by the same oxidant.[1] It is not clear how common such catalytic paths are in reaction of 'non-complementary' systems, where oxidant or reductant has stable oxidation–reduction levels separated by one unit and the other by more than one. Other examples appear amongst oxidations by peroxodisulphate and by molecular oxygen. Like the thiol oxidations, the present system involves novel kinetic forms which facilitate mechanistic inference.

Oxidation of hydroxylamine by excess of cyanoferrate(III) [equation (1)] has been suggested[3] as a method for hydroxylamine analysis. Anderson has

$$2NH_2OH + 2Fe(CN)_6^{3-} = N_2 + 2Fe(CN)_6^{4-} + 2H_3O^+ \quad (1)$$

confirmed[4] the stoicheiometric character of the reaction. He also found that the reaction is catalysed by copper(II) and inhibited in the presence of edta, pyrophosphate, or cyanide. Qualitative observation of the catalysis was made[5] long ago.

EXPERIMENTAL

Reagents.—The following procedures produced little or no change in the rate of reaction: (*a*) for AnalaR potassium cyanoferrate(III), repeated recrystallization from aqueous alcohol or water, including recrystallization from solutions containing low concentrations (*ca.* 10^{-3} mol dm^{-3}) of edta or of potassium cyanide; (*b*) for hydroxylamine, use of the recrystallized chloride or phosphate salt[6] or the free base, generated by thermal decomposition of the phosphate on a vacuum system; and (*c*) for water for recrystallization and for reaction solutions, either passage through a mixed-bed ion exchange column or redistillation of a good grade of distilled water from alkaline permanganate in an all-glass still.

Hydroxylamine analysis was by the bromatometric method,[7] confirmed by a colorimetric method involving oxidation to nitrate and diazotisation[8] or acid–base titration. Potassium cyanoferrate(III) concentrations were based on weight of dry salt, checked by the absorbance at 410 or 420 nm ($\varepsilon = 967$ and 1000 dm^3 cm^{-1} mol^{-1} respectively). Equation (1) is valid for solutions in the presence and absence of oxygen, with or without low concentrations of ethylenediaminetetra-acetic acid (edta), nitrilotriacetic acid (nita), or potassium cyanide. Analysis, by atomic absorbance, of the iron and copper content of one particular batch of reagents, gave the results shown in Table 1.

TABLE 1

Reagent	10^6(Mole metal)/(Mole reagent) Fe	Cu
$(NH_3OH)_3PO_4$	10	12
NaH_2PO_4	7·4	3·7
Na_2HPO_4	5·1	3·7
Borax	75	6
edta	34	6·4
$K_3Fe(CN)_6$		14
Water	$10{\cdot}5 \times 10^{-8}$	$1{\cdot}8 \times 10^{-8}$

Rates of Reaction.—Rates of reaction of cyanoferrate(III) were measured from the decrease in absorbance at 410 or 420 nm by use of Unicam SP 500 and 800 instruments or a Shimadzu QR50 spectrometer, with the temperature controlled to within ±0·1 K. The pH of reaction solutions was maintained with buffers [borate, phosphate, 2-amino-2-hydroxymethylpropane-1,3-diol (tris), or acetate]. For the faster reactions, and those in controlled atmospheres, a simple H-shaped vessel was used. Rates were also measured by the pH-stat method in another laboratory and with different sources of reagents. A Radiometer Titrigraf maintained constant pH by repeated addition of either NaOH or $Ba(OH)_2$ solution from an 0·5 ml syringe, without other buffer. Entry of carbon dioxide from the atmosphere was prevented by use of CO_2-free nitrogen or oxygen. Measurements by the two procedures do not overlap entirely but all the more significant conclusions have been checked both ways. In particular, addition of carbonate to reaction solutions did not alter the rates of reaction unless it caused change of pH.

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RESULTS AND DISCUSSION

Rates in the Presence of Efficient Complexing Reagents.—Initial rates of reaction, measured spectrophotometrically in the presence of edta, show first-order dependence (Table 2) on the concentration of added iron(III) edta and no dependence on that of copper(II) edta, at pH 9·1 and 6·9. The values of *b* correlate well with values of *a* and with estimates (from atomic absorbance) of the *iron* present as contaminant in the reaction components.

TABLE 2

$10^3[\mathrm{Fe(CN)_6}^{3-}] = 0{\cdot}5\,\mathrm{M}$; $10^5[\mathrm{edta}] = 5{\cdot}0\,\mathrm{M}$; $0 \leqslant 10^6[\mathrm{M(edta)}] \leqslant 2{\cdot}5\,\mathrm{M}$ ($\mathrm{M} = \mathrm{Cu^{II}}$ or $\mathrm{Fe^{III}}$)

$$-\mathrm{d}[\mathrm{Fe(CN)_6}^{3-}]/\mathrm{d}t = a[\mathrm{Fe^{III}(edta)}] + b + 0[\mathrm{Cu^{II}(edta)}]$$

pH	Buffer	$10^3[\mathrm{NH_2OH}]/\mathrm{M}$	10^2a	10^8b
9·2	Borate	1·00	7·5 ± 1·8	4·2 ± 2·2
6·9	Phosphate	2·00	6·1	0·6

Whenever edta or nita is present at appreciable concentration in reacting systems, rates of reaction show zeroth-order dependence on cyanoferrate(III) concentration although the destruction of hydroxylamine requires the presence of this oxidant. Thus the apparent rate of acid production at pH 9·6 from hydroxylamine is *ca.* 1% of the rate in presence of 10^{-3} mol dm^{-3} cyanoferrate(III). This residual rate was similar to the rate of entry of $\mathrm{CO_2}$ from the atmosphere. The rate falls to a similarly low value with disappearance of the cyanoferrate(III) colour from reaction solutions.

The reaction rates are of the first order (rate coefficient, k) in hydroxylamine concentration as shown by the ordinary integrated rate plots and by initial rate measurements with varying hydroxylamine concentration, when the latter did not significantly change the concentration of the iron–edta complex. The rate coefficients measured with virtually constant concentration of trace impurities were scarcely altered by replacement of edta by nita. This is illustrated by the values shown in Table 3 obtained at pH 9·2 and 25 °C with 10^{-3} mol dm^{-3} $\mathrm{Fe(CN)_6}^{3-}$ and iron contributed only through the reagent impurity levels. The rate law is thus (2) where $\Sigma[\mathrm{FeY}]$ is the sum of the

$$-\mathrm{d}[\mathrm{Fe(CN)_6}^{3-}]/\mathrm{d}t = k_\mathrm{a}\Sigma[\mathrm{FeY}][\mathrm{NH_2OH}] \qquad (2)$$

concentrations of the iron(II) and iron(III) complexes with edta or nita. At 25 °C, k_a has the values 31 (at pH 6·9) and 87 (at pH 9·1) l mol^{-1} s^{-1}.

TABLE 3

$10^3[\mathrm{NH_2OH}]/\mathrm{M}$	$10^3[\mathrm{edta}]/\mathrm{M}$	$10^3[\mathrm{nita}]/\mathrm{M}$	$10^4k/\mathrm{s}^{-1}$
2·14	0·04	0·00	1·06
2·14	0·08	0·00	1·17
1·00	0·00	0·10	0·96
1·00	0·00	0·50	1·00

Rates in the Absence of Efficient Complexing Reagents.—Initial rates of reaction, measured spectrophotometrically, increase linearly (Table 4) on addition of copper(II) salts at low concentrations, at pH 9·1 and 6·9. Addition of $\mathrm{Co^{2+}}$, $\mathrm{Ni^{2+}}$, $\mathrm{Mn^{2+}}$, $\mathrm{Zn^{2+}}$, and $\mathrm{Cr^{3+}}$ salts produced no increases in rate greater than 1% of that due to copper at similar concentration. With $\mathrm{Fe^{2+}}$ or $\mathrm{Fe^{3+}}$ there were minor *decreases* in reaction rate, *e.g.*, 25% on addition of 10^{-5}M-Fe to solutions containing 3×10^{-7}M-Cu. Variable rates of reaction in the absence of *added* copper were found and attributed to variable copper impurity levels. These rates correlate moderately with estimates (by atomic absorbance) of the copper content. Thus for the experiments at pH 9·1 above, the estimated copper impurity was $9{\cdot}0 \times 10^{-8}$ mol dm^{-3}. The rate without added copper is consistent with the presence of 7×10^{-8} mol dm^{-3} copper.

TABLE 4

$10^3[\mathrm{Fe(CN)_6}^{3-}] = 0{\cdot}5\,\mathrm{M}$; $\mathrm{Cu^{II}}$ added at up to 5×10^{-7} mol dm^{-3}

$$-\mathrm{d}[\mathrm{Fe(CN)_6}^{3-}]/\mathrm{d}t = a[\mathrm{Cu^{II}}] + b$$

pH	Buffer	$10^3[\mathrm{NH_2OH}]/\mathrm{M}$	a	10^6b
9·2	Borate	2·00	42·3 ± 2·7	3·06 ± 0·50
6·9	Phosphate	1·00	8·9 ± 0·5	0·7 ± 0·1

Rates of reactions under these conditions obey the rate law (3), both through particular reactions and in

$$-\mathrm{d}[\mathrm{Fe(CN)_6}^{3-}]/\mathrm{d}t = k_\mathrm{b}\Sigma[\mathrm{Cu}][\mathrm{NH_2OH}][\mathrm{Fe(CN)_6}^{3-}] \qquad (3)$$

terms of initial rate measurements. The measurements of k_b shown in Table 5 by the latter method at 25 °C demonstrate this.

TABLE 5

pH	$10^3[\mathrm{NH_2OH}]/\mathrm{M}$	$10^3[\mathrm{Fe(CN)_6}^{3-}]/\mathrm{M}$	$10^{-7}k_\mathrm{b}/$ l^2 mol^{-2} s^{-1}
9·1	2·00	0·50	3·5
9·1	2·00	0·25	3·8
9·1	1·00	0·50	$3{\cdot}6_5$
6·9	1·00	0·50	1·8

Effects of Reaction Products.—Substitution in cyanoferrate(II) by hydroxylamine has been reported.[9] In confirmation, it was found that dilute (10^{-4} mol dm^{-3}) solutions of potassium cyanoferrate(II) react with hydroxylamine (10^{-3} mol dm^{-3}) at pH 9 to give yellow solutions ($\lambda_{\max.}$ 430 nm) without detectable pH change. The reaction is at least ten times slower than the cyanoferrate(III) reaction under comparable conditions. Solutions of identical u.v. and visible absorption spectrum were formed at similar rates from cyanoferrate(III)–hydroxylamine reaction solutions, with excess of hydroxylamine. The yellow solutions were subject to (slow) oxidation by molecular oxygen, or (rapid) oxidation by cyanoferrate(III). In the latter case, 1·00 mol of cyanoferrate(III) is consumed per mol of cyanoferrate(III) consumed in the *initial* hydroxylamine reaction without pH change. The absorption peak at 430 nm is replaced by one at 318 nm. Equations (4) and (5) are consistent with these observations,

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[9] W. Hieber, R. Nast, and E. Proeschel, *Z. anorg. Chem.*, 1948, **256**, 159.

but products have not been isolated. Addition of more

$$\mathrm{Fe(CN)_6^{4-} + NH_2OH \longrightarrow Fe(CN)_5NHOH^{4-} + HCN} \qquad (4)$$

$$\mathrm{Fe(CN)_5NHOH^{4-} + Fe(CN)_6^{3-} \longrightarrow Fe(CN)_5NHOH^{3-} + Fe(CN)_6^{4-}} \qquad (5)$$

cyanoferrate(III) resulted in acid production at rates only 5—10% higher than those in the absence of the substitution product. Thus the products of these processes have no significance in the normal oxidation mechanism.

Aquopentacyanoferrates are thought to be important in the mechanisms followed by some other $\mathrm{Fe(CN)_6^{3-}}$ systems.[10] Addition of low concentrations of (i) aquopentacyanoferrate(II), prepared by Hofmann's method,[11] or (ii) potassium ferrocyanide solutions, not only fresh but also 'aged', and shortly after exposure to sunlight in a Pyrex vessel (with formation of monomeric pentacyanoferrate highly probable [12]) led to no change of the rate of reaction by more than 10%.

Mechanisms of Reaction.—Reaction with chelating species present. Both edta and nita eliminate catalysis of this oxidation by copper and introduce catalysis by the iron complex. The effective catalyst cannot be the aquated metal ion because the stability constants [13] for the complexes with these reagents differ by orders of magnitude and the rates do not. Catalysis by reaction products, including aquopentacyanoferrates (which can form under some conditions [14]) is unimportant. The similarity of rates in the presence of edta and nita requires that these ligands have little influence on the reactivity with hydroxylamine. A similar situation has been reported [15] for a number of magnesium complexes.

A reaction mechanism consistent with the observations involves equations (6)—(9) in which $\mathrm{M^+}$, M are

$$\mathrm{M^+ + NH_2OH \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} M^+(NH_2OH)} \qquad (6)$$

$$\mathrm{M^+(NH_2OH) + Fe(CN)_6^{3-} + H_2O \xrightarrow{k_2} M^+(NH_2O) + Fe(CN)_6^{4-} + H_3O^+} \qquad (7)$$

$$\mathrm{M^+(NH_2O) + NH_2OH \xrightarrow{k_3} M + N_2 + H_3O^+ + H_2O} \qquad (8)$$

$$\mathrm{M + Fe(CN)_6^{3-} \xrightarrow{k_4} M^+ + Fe(CN)_6^{4-}} \qquad (9)$$

written to represent the $\mathrm{Fe^{III}}$ and $\mathrm{Fe^{II}}$ complexes of edta or nita. If the rates of steps (7)—(9) are high enough so that the reaction rate is limited by k_1, the observed rate law is predicted, apart from the (small) acidity dependence, which may be due to protonation of $\mathrm{NH_2OH}$. Thus, for edta, k_1 is *ca.* 90 l mol^{-1} s^{-1} at 25 °C (pH 9·1).

Reaction without chelating species. If the above reaction sequence is adopted, but with $\mathrm{M^+}$, M representing $\mathrm{Cu^{II}}$ and $\mathrm{Cu^{I}}$ species, the rate law is again accommodated provided (7) is now rate limiting. The equilibrium constants for (6) are known,[16] and correspond to *ca.* 33% formation of the $\mathrm{Cu^{II}(NH_2OH)}$ complex and *ca.* 4% of $\mathrm{Cu^{II}(NH_2OH)_2}$. Again the mechanism gives no explicit treatment of the small variation of rate with pH. From use of known equilibrium constants, the rate coefficient k_2 is given by equation (10). The reduction in rate on addition of

$$\begin{aligned} k_2 &= k_b \Sigma\mathrm{Cu}/[\mathrm{Cu^{II}(NH_2OH)}] \\ &= 1{\cdot}1 \times 10^8\ \mathrm{l\ mol^{-1}\ s^{-1}} \end{aligned} \qquad (10)$$

$\mathrm{Fe^{II}}$ or $\mathrm{Fe^{III}}$, though small, appears genuine. It may be explained as arising from competition for an intermediate in the reaction process, as for example through equations (11) and (12). We suggest that the e.s.r.

$$\mathrm{M^+(NH_2O) + Fe^{II} + H_3O^+ \longrightarrow M^+(NH_2OH) + Fe^{III} + H_2O} \qquad (11)$$

$$\mathrm{Fe^{III} + Fe(CN)_6^{4-} \longrightarrow Fe^{II} + Fe(CN)_6^{3-}} \qquad (12)$$

spectrum observed [2] in the presence of carbonate arises from a side reaction competing with (8) and thus not altering the present rate measurements. Equation (8) in the mechanism involves much geometrical rearrangement and is unlikely to be a single step. The available evidence points to the presence of a reaction product after the rate-limiting step which may be subject to competition, and eliminates some other suggestions. Further work is needed. Rates of reaction of the same order as those above in the absence of efficient complexing agents have been reported [17] without discovery of copper-ion catalysis. The major experimental results may be reinterpreted on the present basis.

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