

Iron(II) Catalysis in the Oxidation of the Aquopentacyanoferrate(II) Complex by Molecular Oxygen

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Oxidation of $Fe(CN)_5H_2O^{3-}$ by molecular oxygen has been shown to be strongly catalyzed by traces of ferrous ions formed from the thermal decomposition of the reactant. The observed rate law for the catalytic reaction was

$$-\frac{d[Fe(CN)_5H_2O^{3-}]}{dt} = k_3[Fe(CN)_5H_2O^{3-}][O_2][Fe^{2+}_{aq}]$$

with $k_3 = 5.6 \pm 0.1 \times 10^6 M^{-2} s^{-1}$ at $25^\circ C$, $\mu = 0.10 M$ lithium perchlorate, pH 4.50.

The influence of pH, temperature and ionic strength and of several bivalent cations on the reaction rates were also investigated. A mechanism is proposed, based on formation of an intermediate or activated complex of the type $[Fe(CN)_5O_2Fe_{aq}]^-$.

Introduction

The reactions of transition metal complexes with molecular oxygen have been shown^{1–4} to be strongly dependent on the properties of the metallic ion, as well as on the chemical environment, including the ligands, electrolytes and the solvent^{5–8}. In some cases, as in Vaska's⁹ and in some cobalt(II) complexes^{3,10–12}, absorption of molecular oxygen takes place in reversible way, yielding stable and well characterized adducts. However, in most of the cases, oxidation seems to occur irreversibly, producing peroxides or oxides as final products.

Absorption of oxygen by cyanocomplexes of cobalt(II) has been extensively investigated in recent years^{13,14} and interesting results, such as the isolation and X-Ray structure of mononuclear $Co(CN)_5O_2^{3-}$ complexes have been reported¹⁵. For the cyanocomplexes of iron(II), although their reactivity with respect to molecular oxygen is known since the beginning of this century^{16,17}, little has been done to understand the nature and mechanism of these important reactions.

The ion aquopentacyanoferrate(II) seems to be especially important for this kind of study, considering the expected similarities with other oxygen sensitive

pentacyano and pentaamminecomplexes of cobalt(II) and ruthenium(II)^{1–4}. The aquopentacyanoferrate(II) ion is also the intermediate product of the thermal and photochemical decomposition of ferrocyanide^{18,19} and several pentacyanoferrate(II)²⁰ complexes in aqueous solution.

Usually, most of the work dealing with cyanocomplexes of iron(II) has been carried out without any especial precaution to exclude air. The present investigation has shown, however, that under certain conditions the reaction of $Fe(CN)_5H_2O^{3-}$ with molecular oxygen proceeds with reasonably fast rates and it is apparently one of the sources of errors and irreproducibility frequently reported in the literature^{21,22}.

The kinetics of the reaction of the aquopentacyanoferrate(II) ion with molecular oxygen have been investigated and possible mechanisms are discussed in this paper.

Experimental

The salt $Na_3[Fe(CN)_5NH_3] \cdot 3H_2O$ was prepared from analytical grade sodium nitroprusside, according to the conventional procedure²³. *Anal.* Calcd: C, 18.42; N, 25.77; H, 2.76. Found: C, 18.33; N, 25.57; H, 2.59.

Solutions of aquopentacyanoferrate(II) ($10^{-5} M$) were obtained by careful neutralization of the ammine complex with diluted hydrochloric acid or appropriate buffers (acetate, hydrogen phosphate), under argon atmosphere. Argon was previously treated with aqueous chromium(II) to ensure complete removal of oxidizing impurities present in the gas. Solutions of dissolved oxygen were prepared by bubbling the pure gas into distilled, deionized water at $25.0^\circ C$. Analysis of dissolved oxygen was made by Winckler's method^{24,25} with a reproducibility better than 3%. Analysis of iron(II) was made spectrophotometrically with 1,10-phenanthroline, in the conventional way²⁶.

Potentiometric and pH measurements were made with a Beckman Expandomatic SS-2 pHmeter, at a controlled temperature. Potentiometric titrations of aqueous $Fe(CN)_5H_2O^{3-}$ ($10^{-3} M$) with Ce(IV) or

HCl, were carried out under argon atmosphere, using ultraprecision micrometer syringes.

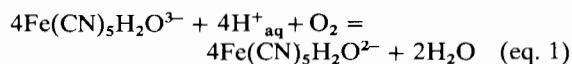
Visible-UV spectra of 2×10^{-5} to $1 \times 10^{-3} M$ solutions of the aquopentacyanoferrate(II) complex were recorded with a Cary 17 spectrophotometer, equipped with a universal absorbance scale. No significant Beer's law deviation was observed in this range of concentration at 440 nm, the wavelength at the maximum for the first allowed $d-d$ transition in $\text{Fe}(\text{CN})_5\text{H}_2\text{O}^{3-}$.

Reaction rates were measured at 440 nm with a Cary 14 spectrophotometer, fitted with thermostated cell compartments ($\pm 0.1^\circ \text{C}$) or with a Durrum D-110 stopped-flow instrument. 5.0 pathlength cells and a 0 to 0.1 absorbance scale were employed in the kinetic experiments with $3 \times 10^{-5} M$ solutions of $\text{Fe}(\text{CN})_5\text{H}_2\text{O}^{3-}$, carried out in the Cary 14 spectrophotometer. Solutions were mixed with the aid of a thermostated syringe, fitted with a long, dispersion teflon needle.

Results and Discussion

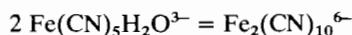
Characterization of the Reactants and Products

The stoichiometry of oxidation of $\text{Fe}(\text{CN})_5\text{H}_2\text{O}^{3-}$ by molecular oxygen has been previously established by Kenney²⁷ *et al.*, according to equation 1.



The changes observed in the spectrum of the reacting mixture (Figure 1) are also consistent to the stoichiometry above. As can be seen in Figure 1, the disappearance of the peak centered at 440 nm ($\epsilon = 640 M^{-1} \text{cm}^{-1}$) in the $\text{Fe}(\text{CN})_5\text{H}_2\text{O}^{3-}$ complex is followed by the appearance of two new peaks at 394 nm ($\epsilon = 750 M^{-1} \text{cm}^{-1}$) and at 340 nm ($\epsilon = 750 M^{-1} \text{cm}^{-1}$) characteristic of monomeric²⁸ $\text{Fe}(\text{CN})_5\text{H}_2\text{O}^{2-}$.

Although similar changes in the spectrum of $\text{Fe}(\text{CN})_5\text{H}_2\text{O}^{3-}$ have been recently assigned²⁹ to the dimerization process



such assignment was not considered in the present work due to the following reasons: (i) In the complete absence of oxygen and oxidizing agents, no evidence for the peaks at 394 nm and 340 nm has been observed, both in hydrogenphosphate and in acetate buffers; (ii) The rates of disappearance of the mononuclear $\text{Fe}(\text{CN})_5\text{H}_2\text{O}^{3-}$ complex (440 nm) forming the product that absorbs at 394 and 340 nm, are proportional to the concentration of dissolved oxygen, as will be demonstrated in this work; (iii) Using the dimerization constant of $90 M^{-1}$ determined by Emschwiller³⁰, it seems obvious that at the dilution level employed in this work ($10^{-5} M$), the amount of the dimeric species

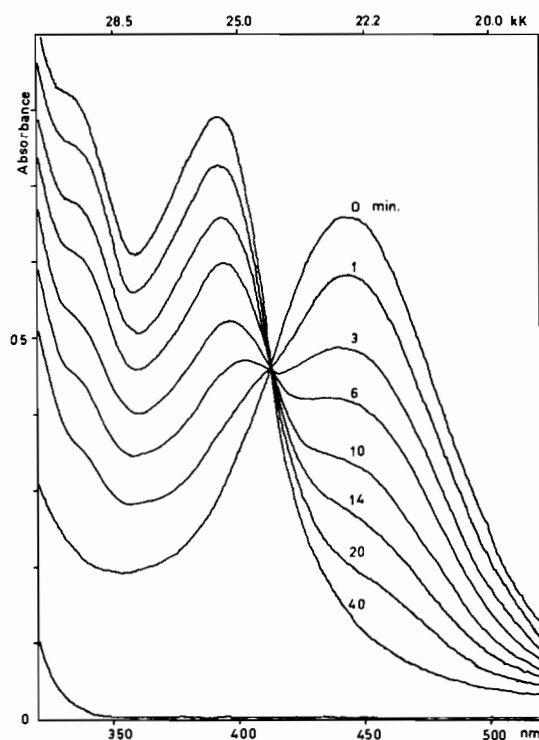


Figure 1. Changes in the visible-uv spectra of $\text{Fe}(\text{CN})_5\text{H}_2\text{O}^{3-}$ during the oxidation with molecular oxygen.

must be insignificant; (iv) The absence of the dimer $\text{Fe}_2(\text{CN})_{10}^{6-}$ in the product has been confirmed according to Emschwiller and Jørgensen's³¹ procedure. After the *complete disappearance* of the peak at 440 nm of monomeric $\text{Fe}(\text{CN})_5\text{H}_2\text{O}^{3-}$, the final solution was treated with an excess of bromine, which was removed by passing a stream of argon into the system. The spectrum of the final solution resulted virtually unchanged. If dimeric species were present, the violet $\text{Fe}_2(\text{CN})_{10}^{4-}$ complex with a strong absorption at 563 nm ($\epsilon \sim 10^3 M^{-1} \text{cm}^{-1}$) would be observed³¹, but that was not the case; (v) The spectrum of the product in the reaction of $\text{Fe}(\text{CN})_5\text{H}_2\text{O}^{3-}$ with molecular oxygen is identical to that reported by Espenson and Wolenuk²⁸ for the monomeric $\text{Fe}(\text{CN})_5\text{H}_2\text{O}^{2-}$ complex.

Starting from the aminopentacyanoferrate(II) complex, Kenney *et al.*²⁷ observed that oxidation takes place more rapidly in acid solutions, being considerably retarded in the presence of bases. In order to obtain a better understanding of the pH effects on the reaction rates, the pK_a of the aquopentacyanoferrate(II) complex was determined at the same conditions of the kinetics experiments, *i.e.*, $T = 25.0^\circ \text{C}$, $\mu = 0.100 M$ lithium perchlorate. The procedure adopted in this case was the following: a sufficient amount of $\text{Na}_3[\text{Fe}(\text{CN})_5\text{NH}_3] \cdot 3\text{H}_2\text{O}$ was dissolved in distilled, deionized water, under argon atmosphere, to give a $2 \times 10^{-3} M$ solution

of the complex. After 20 minutes in the thermostated bath (25.0°C), with argon being continuously passed through the system, the complex was carefully titrated with standardized solution of HCl , using a combined glass microelectrode for pH measurements. The readings were taken only after complete pH stabilization and were extended to at least three times beyond the first sharp equivalence point, corresponding to neutralization of free ammonia.

The curve of acid consumption for the aquopentacyanoferrate(II) complex is shown in Figure 2 (curve a), in comparison to that of the S-bonded dimethylsulfoxide pentacyanoferrate(II) complex³² (curve b) and the free acid dilution curve (curve c). Curves b and c are very similar and indicate that the consumption of protons by the dimethylsulfoxide complex is practically negligible.

Due to the absence of inflections in the titration curve of the aquopentacyanoferrate(II) complex, as in the case of the ferrocyanide complex studied by Jordan and Ewing³³, the determination of pK_a cannot be made by simple inspection of the experimental curve. However, Speakman³⁴ has described a method whereby the ionization constants of weak dibasic acids can be

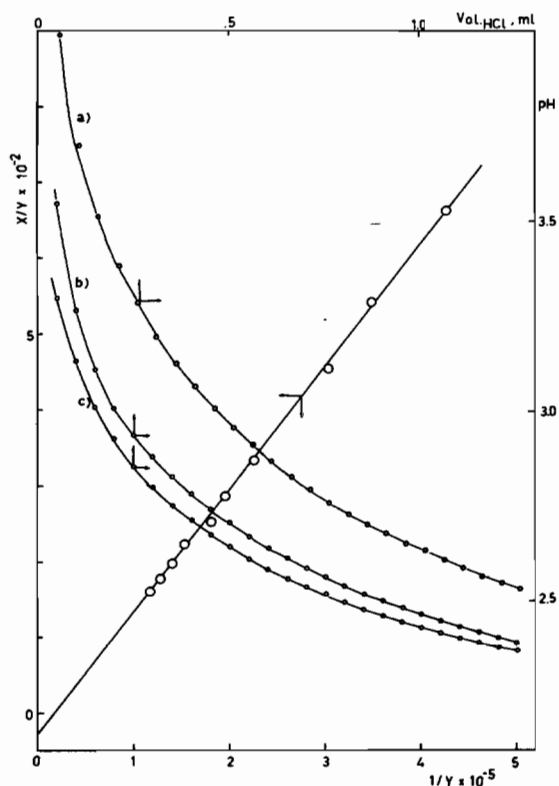
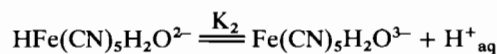
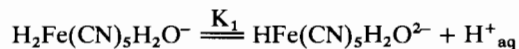


Figure 2. Titration curves of $\text{Fe}(\text{CN})_5\text{H}_2\text{O}^{3-}$ (curve a), $\text{Fe}(\text{CN})_5\text{SO}(\text{CH}_3)_2^{3-}$ (curve b) and water (curve c), with HCl , 0.0400N . Plot of X/Y vs. $1/Y$, used in the evaluation of pK_2 of $\text{HFe}(\text{CN})_5\text{H}_2\text{O}^{2-}$.

determined from inflectionless titration curves of the type obtained in this study.

Applying Speakman's treatment to the equilibria expressed by



$$K_1 = \frac{[\text{HFe}(\text{CN})_5\text{H}_2\text{O}^{2-}][\text{H}^+_{\text{aq}}]}{[\text{H}_2\text{Fe}(\text{CN})_5\text{H}_2\text{O}^-]} \quad (\text{eq 2.1})$$

$$K_1K_2 = \frac{[\text{Fe}(\text{CN})_5\text{H}_2\text{O}^{3-}][\text{H}^+_{\text{aq}}]^2}{[\text{H}_2\text{Fe}(\text{CN})_5\text{H}_2\text{O}^-]} \quad (\text{eq 2.2})$$

considering the charge balance,

$$[\text{Na}^+] + [\text{H}^+] = [\text{Cl}^-] + [\text{OH}^-] + 3[\text{Fe}(\text{CN})_5\text{H}_2\text{O}^{3-}] + 2[\text{HFe}(\text{CN})_5\text{H}_2\text{O}^{2-}] + [\text{H}_2\text{Fe}(\text{CN})_5\text{H}_2\text{O}^-] \quad (\text{eq 2.3})$$

and calling

$$b = [\text{Fe}(\text{CN})_5\text{H}_2\text{O}^{3-}] + [\text{HFe}(\text{CN})_5\text{H}_2\text{O}^{2-}] + [\text{H}_2\text{Fe}(\text{CN})_5\text{H}_2\text{O}^-] \quad (\text{eq 2.4})$$

$$L = [\text{Cl}^-] + [\text{OH}^-] - [\text{H}^+]$$

equation 2.5 can be obtained by combining equations 2.1–2.4.

$$\left(\frac{2b}{L} - 1\right)[\text{H}^+]^2 = \left(1 - \frac{b}{L}\right)[\text{H}^+][K_1 + K_1K_2] \quad (\text{eq 2.5})$$

Eq 2.5 can be represented by

$$Y = K_1X + K_1K_2 \quad (\text{eq 2.6})$$

Dividing eq 2.6 by K_1Y ,

$$X/Y = 1/K_1 - K_2/Y \quad (\text{eq 2.7})$$

A typical plot of X/Y versus $1/Y$ is shown in Figure 2. Excellent linear correlations were obtained in several repetitive determinations, with an estimated value of pK_2 equal to 2.75 ± 0.1 . K_2 refers to a concentration dissociation constant valid at the ionic strength of 0.10M . Corrections of the measured hydrogen ion activities to the corresponding values of concentrations, using the extended Debye-Hückel equation, only slightly influenced pK_2 . Determination of pK_1 were very unsatisfactory using either eq 2.6 or eq 2.7, due probably to the small value expected for the second protonation constant, ($\text{pK}_1 \leq 1$).

Kinetics of the Reactions of $\text{Fe}(\text{CN})_5\text{H}_2\text{O}^{3-}$ with Dissolved O_2

The rates of disappearance of $\text{Fe}(\text{CN})_5\text{H}_2\text{O}^{3-}$ in the presence of molecular oxygen in excess obey a first order rate law, during at least three half lives.

The following procedure has been employed in the kinetics experiments: a sufficient amount of $\text{Fe}(\text{CN})_5\text{NH}_3^{3-}$ was submitted to aquation³⁵ in a buffered medium at controlled ionic strength, under argon, to give a final concentration of $2.5 \times 10^{-4}\text{M}$ for the aquo-

pentacyanoferrate(II) complex. After 10 to 20 minutes in the dark, 1.40 ml of the $\text{Fe}(\text{CN})_5\text{H}_2\text{O}^{3-}$ solution was mixed, under thermostated conditions, with 12.6 ml of distilled, deionized water containing dissolved oxygen, in a 5 cm pathlength cylindrical cell. The changes in absorbance in the range of 0.1 to 0.01 were recorded at 440 nm with the Cary 14 spectrophotometer.

The initial experiments were carried out in the presence of phosphate, at 25°C, $[\text{O}_2] = 1.8 \times 10^{-4} \text{ M}$, the pH varying from 7 to 3 by adding perchloric acid. The dependence of the observed rate constants on the pH is illustrated in Figure 3 (black circles, 1–8). An attempt to reproduce those values, using acetate instead of phosphate buffers, can be seen in the same figure (empty circles, 9–16).

The randomness observed in the rates measured in acetate media was found to be associated with aging processes that start during the aqutation of the aminopentacyanoferrate(II) complex. Considering that the phosphate and acetate buffers have different complexing powers, some of the experiments carried out in acetate media were repeated in the presence of small amounts of EDTA ($1 \times 10^{-3} \text{ M}$). The results are shown in Figure 3 (half filled circles, 17–20).

These initial experiments clearly demonstrated that oxidation of $\text{Fe}(\text{CN})_5\text{H}_2\text{O}^{3-}$ by molecular oxygen

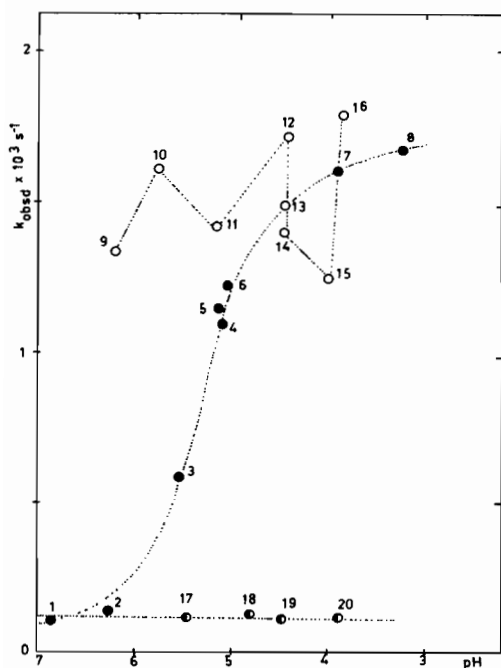


Figure 3. Observed rate constants for the oxidation of $\text{Fe}(\text{CN})_5\text{H}_2\text{O}^{3-}$ by O_2 , in phosphoric media (expts. 1–8), acetic media (expts. 9–16) and acetic + EDTA media (17–20), at 25°C and $[\text{O}_2] = 1.8 \times 10^{-4} \text{ M}$.

is strongly inhibited by complexing agents in aqueous solution. Pursuant to these observations, the influence of several most probable impurities in the reaction rates was tested. The bivalent alkaline earth, zinc, manganese, cobalt and nickel cations at 10^{-5} M had no influence on the reaction rates. Copper(II) ions, at $1 \times 10^{-5} \text{ M}$, increased the observed rate constant measured in acetate media by ca. 50%. Iron(II) ions were found to be ten times more effective than copper(II) as catalysts the oxidation of $\text{Fe}(\text{CN})_5\text{H}_2\text{O}^{3-}$ by molecular oxygen.

Decomposition of the aquopentacyanoferrate(II) complex forming ferrous ions has been reported¹⁸ to occur with a first order rate constant of $9.25 \times 10^{-6} \text{ s}^{-1}$ at 40°C, pH 4.0. Although this aging process occurs with a rate considerably smaller than the rates of oxidation of $\text{Fe}(\text{CN})_5\text{H}_2\text{O}^{3-}$ by molecular oxygen, the traces of ferrous ions formed during the initial time have shown to be sufficient to account for the randomness observed in experiments 9–16 (Figure 3). The influence of phosphate and EDTA on the reaction rates can be explained by complexation of ferrous and ferric ions, inhibiting their catalytic activity.

A complete set of experiments showing the dependence of oxygen and ferrous ions concentrations (expt.

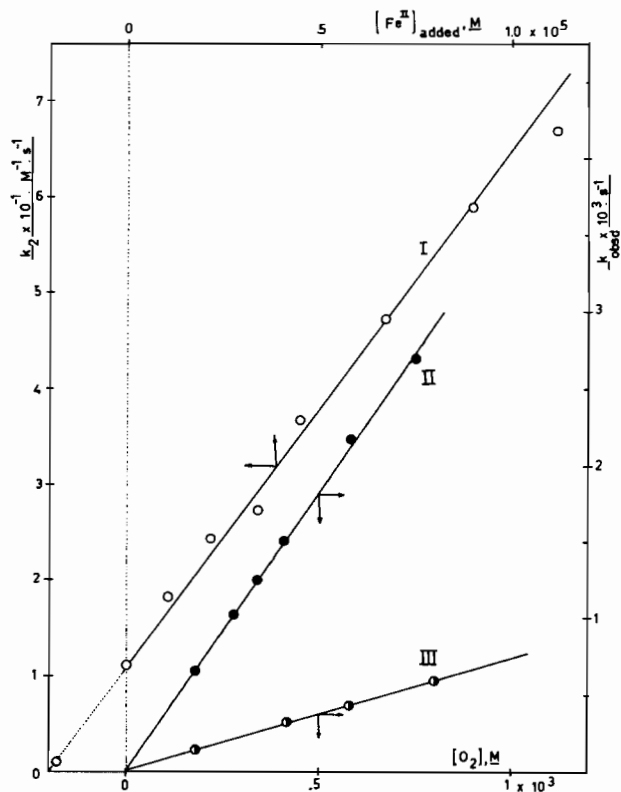


Figure 4. Dependence of the rates of oxidation of $\text{Fe}(\text{CN})_5\text{H}_2\text{O}^{3-}$ on ferrous ions (curve I) and oxygen (curves II and III) concentrations (conditions: see text).

TABLE I. Rates of Oxidation of $\text{Fe}(\text{CN})_5\text{H}_2\text{O}^{3-}$ by Dioxygen.

Expt. No.	T(°C)	μ^a (LiClO ₄)	pH	[O ₂] $\times 10^4 M$	[Fe(II)] add $\times 10^6 M$	k_{obs} $\times 10^3 \text{ s}^{-1}$	k_3^b $\times 10^{-6} M^{-2} \text{ s}^{-1}$
21	25.0	0.10	4.50	1.8	0.0	2.0	5.7
22	25.0	0.10	4.50	1.8	1.1	3.3	5.8
23	25.0	0.10	4.50	1.8	2.2	4.4	5.8
24	25.0	0.10	4.50	1.8	3.4	4.9	5.1
25	25.0	0.10	4.50	1.8	4.5	6.6	5.6
26	25.0	0.10	4.50	1.8	6.7	8.5	5.4
27	25.0	0.10	4.50	1.8	9.0	10.6	5.4
28	25.0	0.10	4.50	1.8	11.2	12.0	5.1
29	25.0	0.10	4.50	4.2	0.0	3.0	5.5
30	25.0	0.10	4.50	5.7	0.0	4.3	5.7
31	25.0	0.10	4.50	8.0	0.0	5.9	5.7
32	25.0	0.10	4.50	2.8	4.4	10.5	5.8
33	25.0	0.10	4.50	3.4	4.4	12.7	5.8
34	25.0	0.10	4.50	4.1	4.4	15.1	5.7
35	25.0	0.10	4.50	5.8	4.4	21.8	5.8
36	25.0	0.10	4.50	7.5	4.4	26.9	5.6
37	25.0	0.10	3.40	4.1	4.6	19.8	7.3
38	25.0	0.10	3.80	4.7	4.7	17.6	5.6
39 ^c	25.0	0.10	4.50	4.2	4.6	15.8	5.7
40	25.0	0.10	5.40	4.4	4.6	16.5	5.7
41 ^c	25.0	0.10	4.50	4.2	4.6	16.0	5.7
42	25.0	0.43	4.50	4.2	4.3	8.3	3.1
43	25.0	0.86	4.50	4.3	4.3	5.9	2.2
44	12.5	0.10	4.50	4.2	4.7	6.4	2.3
45	18.3	0.10	4.50	4.3	4.7	9.4	3.2
46 ^d	25.0	0.10	4.50	4.1	4.3	14.9	5.7
47	31.3	0.10	4.50	4.1	4.7	20.0	7.3
48	39.4	0.10	4.50	3.5	4.6	31.0	13.3

^a Acetate buffer, $1 \times 10^{-2} M$, $[\text{Fe}(\text{CN})_5\text{H}_2\text{O}^{3-}] = 3 \times 10^{-5} M$. ^b Calcd from k_{obs} divided by oxygen and corrected ferrous ions concentrations. ^c For expts. 39 and 41, acetate buffer concs. were 0.025 and 0.0025 M , respectively.

^d $[\text{Fe}(\text{CN})_5\text{H}_2\text{O}^{3-}] = 6 \times 10^{-5} M$.

21–36), pH (expt. 37–40), ionic strength (expt. 41 to 43), buffer (expt. 39, 41) and temperature (expt. 44–48) on the rates of oxidation of $\text{Fe}(\text{CN})_5\text{H}_2\text{O}^{3-}$ by molecular oxygen can be seen in Table I.

The time after dissolution of $\text{Na}_3[\text{Fe}(\text{CN})_5\text{NH}_3] \cdot 3\text{H}_2\text{O}$ and before final mixing was maintained in the range of 15 ± 2 minutes, in order to provide a reproducible level of catalytic ferrous ions in the reaction mixture. From the plots shown in Figure 4 one can conclude that the oxidation of $\text{Fe}(\text{CN})_5\text{H}_2\text{O}^{3-}$ is rigorously first order both in $\text{Fe}^{2+}_{\text{aq}}$ and in O_2 concentrations. Extrapolation of plot I to the rate constant of the non-catalytic process (Figure 3), indicated that the ferrous ions concentration generated from the decomposition of $\text{Fe}(\text{CN})_5\text{H}_2\text{O}^{3-}$, $3 \times 10^{-5} M$, is equal to $1.8 \times 10^{-6} M$, under the conditions of this work. Such an amount of ferrous ions corresponds to a decomposition of ca. 6% of the initial reagent.

By correcting the concentrations of added ferrous ions by the contribution from the decomposition process, the last column of Table I can be obtained, yielding the rate law

$$-\frac{d[\text{Fe}(\text{CN})_5\text{H}_2\text{O}^{3-}]}{dt} = k_3[\text{Fe}(\text{CN})_5\text{H}_2\text{O}^{3-}][\text{O}_2][\text{Fe}^{2+}_{\text{aq}}]$$

with k_3 equal to $5.6 \pm 0.1 \times 10^6 M^{-2} \text{ s}^{-1}$.

The constant values of the reaction rates above pH 3.8 are consistent with the presence solely of non-protonated species, as expected from the pK_a of 2.75 of the $\text{Fe}(\text{CN})_5\text{H}_2\text{O}^{3-}$ complex. The small increase of the rate constant at pH 3.40 seems to be associated to the protonation of the reactant.

The decrease of the rate constants with the increasing ionic strength values is consistent to the participation of oppositely charged species in the rate determining steps of the oxidation reaction.

From the temperature dependence experiments, the following activation parameters have been calculated: $\Delta H^\ddagger = 10.8 \pm 0.5 \text{ kcal/mol}$ (45.8 kJ/mol) and $\Delta S^\ddagger = +8 \pm 2 \text{ e.u.}$, for the 3th order reaction.

Mechanisms of Oxidation of $\text{Fe}(\text{CN})_5\text{H}_2\text{O}^{3-}$ with O_2

The oxidation of ferrous ions by molecular oxygen occurs with an immeasurably slow rate (less than 1%

after 1 hour) under the conditions of this work (25°C, $\mu = 0.10M$ LiClO₄, [O₂] = $2 \times 10^{-4}M$, [Fe²⁺_{aq}] = $3 \times 10^{-5}M$, pH 4.50). The expected rate according to the literature³⁶⁻³⁸, has a magnitude of $10^{-9} s^{-1}$ for k_{obs} .

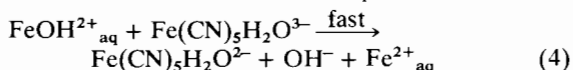
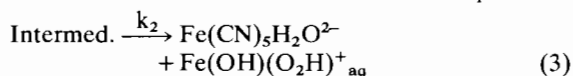
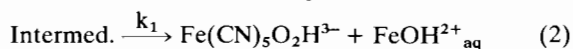
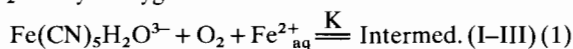
Therefore, the ability of ferrous ions to catalyse the oxidation of Fe(CN)₅H₂O³⁻ by molecular oxygen is a surprising fact which was not predicted from the properties of each reactant separately.

The cooperative effect that happens when Fe(CN)₅H₂O³⁻ and ferrous ions react with molecular oxygen seems to arise from the stabilization of the intermediate or activated complex involving the three reactants. Such activated complex could admit several structures:



Structure I represents an oxygen bridged complex which has many real examples in the chemistry of cyano and aminocomplexes of cobalt¹⁰. Structures II and III could be considered as associated species, favored as is structure I, by the highly positive and negative charges of the reactants.

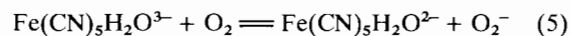
Formation of these species as intermediates or activated complexes is compatible with the time scale for the oxidation process, since both aqueous ferrous ions and Fe(CN)₅H₂O³⁻ are sufficiently labile²⁰. It is also consistent with the observed ionic strength dependence and with the positive activation entropy expected for the case of association of oppositely charged species³⁹. According to these arguments, the following mechanism can be proposed for the oxidation of Fe(CN)₅H₂O³⁻ by dioxygen:



The last reaction, responsible for the catalytic activity of the ferrous ions, has shown to be complete within 15 milliseconds, under the conditions of this work. The second order rate constants for the reduction of ferric ions ($1.0 \times 10^{-5}M$) by Fe(CN)₅H₂O³⁻ at $5.0 \times 10^{-5}M$ and $1.0 \times 10^{-4}M$ ($\mu = 0.10$ LiClO₄, acetate buffer $0.02M$, pH 4.5, 25°C) measured by the stopped-flow technique were $1.0 \times 10^6 M^{-1} s^{-1}$ and $1.1 \times 10^6 M^{-1} s^{-1}$, respectively. In the presence of an excess of ferric ions ($> 1 \times 10^{-4}M$), the disappearance of Fe(CN)₅H₂O³⁻ is masked by formation of prussian blue species and polymeric basic acetates, with dramatic changes in the optical density of the system.

The peroxide products Fe(CN)₅O₂H³⁻ and Fe(OH)(O₂H)⁺_{aq} are expected to react rapidly with Fe(CN)₅H₂O³⁻, in analogy with reaction 4, yielding Fe(CN)₅H₂O²⁻ and aqueous ferrous ions.

From the oxidation potential of $-0.39 V (\pm 0.01V)$ measured for the aquopentacyanoferrate(II) complex at 25°C, $\mu = 0.10$ LiClO₄, pH 4.50 under argon atmosphere, a free energy increase of about 18 kcal/mol can be expected for reaction 5:



It seems therefore that the radical ion mechanism should not be favored in comparison to the associative mechanism proposed in this article. Similar conclusions have been obtained in the case of the oxidation of aqueous ferrous ions by molecular oxygen¹.

The catalytic activity of copper ions can be explained by a similar mechanism postulated for iron(II). However, since even in the case of the oxidation of ferrous ions by O₂, the mechanism remains not completely understood^{38,40-43}, it is probable that many other possibilities could be further included in this work.

The stability of the basic solutions of Fe(CN)₅NH₃³⁻ to oxidation with dioxygen can be explained by the fact that under such conditions, the amount of Fe(CN)₅H₂O³⁻ is strongly reduced by the presence of free ammonia³⁵. Also the catalysis of iron(II) should be inhibited by removal of ferrous or ferric ions as insoluble hydroxide complexes.

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