Reaction of $[Fe_2(CN)_{10}]^{4-}$ with L-Ascorbic Acid†

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The oxidation of L-ascorbic acid by the iron(III) dimeric complex $[Fe_2(CN)_{10}]^{4-}$ in acidic aqueous solution at an ionic strength of 1.0 mol dm^{-3} ($NaClO_4$) has been studied by stopped-flow spectrophotometry. The overall reaction, which entails reduction of both iron(III) centres followed by aquation resulting in the formation of 2 mol of $[Fe(CN)_5(OH_2)]^{3-}$, takes place in three stages. The first is a one-electron reduction to form the mixed-valence iron(III, II) dimer followed by a second one-electron reduction of the other iron(III) centre to form the iron(II) dimer. The third stage which occurs with a very small absorbance change was not studied. The mechanisms for both stages of the reaction are similar and involve formation of an ion triplet $[Fe_2(CN)_{10}]^{n-}\cdot M^+\cdot A^{p-}$ where $n = 4$ or 5 and A^{p-} is the reacting ascorbate species with $p = 1$ or 2. The rate law was found to be of the form (i) where $[A]_T$ is the total concentration of added ascorbate, K_1 and K_2 the acid dissociation constants

$$\text{Rate} = \frac{k'K_1[H^+] + k''K_1K_2}{K_1K_2 + K_1[H^+] + [H^+]^2}[A]_T[\text{complex}] \qquad (i)$$

of ascorbic acid and k' and k'' the pseudo-second-order rate constants. They were found to be 6.44×10^3, 2.48×10^9 and 1.25×10^3, 2.98×10^8 dm^3 mol^{-1} s^{-1} at 19 °C for HA^- and A^{2-} for the first and second stages respectively. The reaction is affected by alkali-metal cations, increasing rate with increasing size of the metal ions: $Li^+ < Na^+ < K^+$.

Redox reactions of L-ascorbic acid are finding ever increasing usage in the food-processing industry, in photoconversion schemes and in titrations using ascorbic acid as a reductant. As a result, knowledge of the kinetic parameters that characterise the rates of ascorbate reductions is desirable.

L-Ascorbic acid (H_2A) forms metal complexes of the type MA and M(HA) depending on the pH used.[2] Apart from chelation through oxygens at carbon atoms 2 and 3, other unusual binding sites are possible at C(2) and O(5).[3] Several kinetic studies[4–7] have been made with a wide range of metal ions and metal complexes and a valuable review has recently appeared.[8] It was found, in general, that these reactions exhibit a characteristic pH dependence which can be related to the acid-dissociation steps of ascorbic acid and/or the hydrolysis equilibria of the oxidant. The reactions of metal complexes with ascorbic acid as with other organic reducing agents can be classified into three basic categories: (*i*) outer-sphere electron transfer, (*ii*) inner-sphere electron transfer, which occurs subsequent to the substitution of a ligand for ascorbate and (*iii*) a bridging mechanism in which ascorbate is bound to a ligand of the complex prior to electron transfer. While L-ascorbic acid reacts mainly *via* an outer-sphere mechanism, inner-sphere electron transfer in its oxidation by metal complexes has been reported.[9,10] These reactions usually involve the formation of an intermediate followed by electron transfer. One reaction of increasing importance is the reduction of chromium(VI) by ascorbic acid. Dixon *et al.*[11] found that oxygen severely retarded this reaction, clean first-order kinetic profiles being obtained in instances where aerobic and anaerobic conditions were used.

The oxidation of L-ascorbic acid by some substituted pentacyanoferrate(III) complexes has been studied.[5,12,13] More recently Gould and co-workers[14] studied the reaction of $[Co_2(CN)_{10}(O_2)]^{5-}$ with ascorbate. They found that the reaction is catalysed markedly and specifically by dissolved copper. It proceeds about 10^5 times more rapidly than estimated for a straightforward outer-sphere process, which was explained in terms of an unusually facile inner-sphere path that predominates.

The di-μ-cyano-bis[tetracyanoferrate(III)] ion has in recent times moved to the forefront of the study of cyanide-bridged binuclear complexes.[1,15] It undergoes a one-electron transfer to form the mixed-valence ion $[Fe_2(CN)_{10}]^{5-}$ in most of its redox reactions with one-electron reductants. The mechanisms are not straightforward outer-sphere reactions but usually involve some sort of ion-pair formation. Both iron-(III) and -(II) cyano complexes are low spin and inert and therefore expected to react with oxidants such as ascorbate by an outer-sphere mechanism. Therefore as part of our continuing interests in the chemistry of $[Fe_2(CN)_{10}]^{4-}$ the reaction with L-ascorbic acid was studied.

Experimental

Materials.—L-Ascorbic acid (BDH) of biochemical grade was used as supplied. All other chemicals were AnalaR grade used as obtained. The $[Fe_2(CN)_{10}]^{4-}$ complex was prepared and purified as described previously.[1] Deionised distilled water was obtained from a Millipore system and used to make up all solutions.

Kinetics.—The rate of the reaction was followed by stopped-flow spectrophotometry using a High-Tech Scientific SF-51 stopped-flow attached to a High-Tech Scientific SU-40 UV/VIS spectrophotometer unit. The machine was attached to a Haake GH constant-temperature water-bath fitted with a Haake D8 circulating pump. The reaction was monitored by the disappearance of the peak at 560 nm where the biggest absorbance change occurred. Ionic strength was regulated (1.0 mol dm^{-3}) by addition of $NaClO_4$ which was standardised by an ion-exchange method, and the pH of the solution was controlled by a citrate–phosphate buffer.[16] Values of pH were

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† Redox chemistry of $[Fe_2(CN)_{10}]^{4-}$. Part 3.[1]

measured using an Orion Research EA920 Expandable Ion Analyzer. In the preparation of kinetic solutions, ascorbic acid was partially neutralised by treatment with the required amount of sodium carbonate to form sodium hydroascorbate. These solutions were made up directly before use. In all cases, the concentration of L-ascorbic acid was at least 40 times in excess of that of the complex.

The absorbance *vs.* time curve measured at 560 nm did not fit a simple exponential decay. This was due to the occurrence of two consecutive reactions, the reduction $Fe^{III}Fe^{III} \longrightarrow Fe^{III}Fe^{II}$, and the subsequent further reduction $Fe^{III}Fe^{II} \longrightarrow Fe^{II}Fe^{II}$. The best wavelength to study these processes is 1277 nm, the peak maximum for the mixed-valence dimer, but this was not possible on our instrument. At 560 nm there is a large decrease in absorbance for the first reaction, but a much smaller change for the second. Attempts to obtain rate data by separate experiments for the early and later stages yielded rate constants which, on reflection, were unsatisfactory (we are indebted to a referee for helpful comments on this point). A fresh set of experiments were carried out in which the whole absorbance *vs.* time curve was analysed in terms of two consecutive first-order reactions by fitting the trace using curve-fitting equations in the kinetic software program (Hi-Tech Scientific IS-1, Rapid Kinetic Software Suite V 1.0a, Hi-Tech Scientific Ltd.). The results, shown in Table 1, are the averages from at least two kinetic runs and varied within error limits of ± 5%. At the high values of the rate of the first stage the error limits were ± 8–10%. Values of k_{obs} for both processes were shown to be directly proportional to $[\text{ascorbic acid}]_T$. Values for the rate constants were obtained using a least-squares analysis program (EXCEL 5.0, Microsoft Corporation, Washington, 1993) as described below.

Results and Discussion

Addition of a colourless solution of sodium hydroascorbate to the complex $[Fe_2(CN)_{10}]^{4-}$ results in the rapid disappearance of the peak of the latter at 560 nm with the formation of a pale yellow species identified from its spectra as $[Fe_2(CN)_{10}]^{6-}$. This is followed by a slower reaction resulting in the formation of an even paler yellow solution which we identified spectroscopically as $[Fe(CN)_5(OH_2)]^{3-}$. Preliminary studies of the reaction of ascorbic acid with the complex indicate that there are three consecutive 'first-order' stages. It is proposed that the first two are successive electron-transfer reactions resulting in reduction of the two iron (III) centres, followed by the third which is interpreted as aquation of the di-μ-cyano-bis[tetracyanoferrate(II)] ion to yield aquapentacyanoferrate(II) which was identified spectroscopically. Calculations based on the equilibrium constant reported by Emschwiller[17] for the dimer–monomer equilibrium confirm that virtually complete dissociation to the monomer is expected at our concentrations.

Table 1 Pseudo-first-order rate constants for the reaction of L-ascorbic acid with the di-μ-cyano-bis[tetracyanoferrate(III)] ion. [ascorbate] = 20 × 10^{-3} mol dm^{-3}; [complex] = 0.17 × 10^{-3} mol dm^{-3}; I = 1.0 mol dm^{-3} ($NaClO_4$); 19.1 °C

	k_{obs}/s^{-1}	
pH	First step	Second step
3.84	46	8.44
4.09	70.2	12.4
4.28	78.7	14.4
4.40	84.4	—
4.55	100	16.2
4.69	113	21.0
4.87	120	21.8
4.99	126	23.1
5.16	132	24.1
5.31	139	24.7
5.53	150	26.9
5.65	160	28.4
5.91	171	31.5
6.14	201	35.1
6.32	228	42.0
6.53	261	49.2
6.75	296	56.3

The third stage occurred with too small an absorbance change for us to obtain sufficiently reproducible kinetics. The reaction has been studied by James and Murray,[18] and their data imply a first-order rate constant of *ca.* 1.4 × 10^{-5} s^{-1} at 25 °C for the conversion of the iron(II) dimer into $[Fe(CN)_5(OH_2)]^{3-}$.

Individual runs showed first-order kinetics in [complex] for both redox stages. The kinetic results of the first and second stages of the reaction show a first-order dependence on the concentration of L-ascorbic acid. Thus the overall rate law has a second-order form (1), in which $[A]_T$ is the total stoichiometric

$$\text{rate} = k[\text{complex}][A]_T \qquad (1)$$

ascorbate concentration. A similar second-order rate law was found for the second stage also.

The rate of the first stage was studied in the range pH 3.6–6.7 and there was a steady increase in k_{obs} with pH as shown in Table 1. The pK_a values of ascorbic acid are 4.03 and 11.93 and so in our pH range we have mainly H_2A and HA^- with a very low concentration of A^{2-}. However it has been established by many workers that in the outer-sphere redox reactions of ascorbic acid the reactivity sequence is $A^{2-} \gg HA^- \gg H_2A$. Thus in the reaction of the thiourea complex $[Fe(CN)_5(tu)]^{2-}$ with ascorbic acid[12] the reactivity of HA^- is *ca.* 600 times greater than that of H_2A. In our system the ratio $[H_2A]/[HA^-]$ is never more than 2.1 : 1 so it can readily be understood why we did not detect reaction by a pathway involving H_2A; to have done so would have required much more acidic conditions. As in previous investigations[1,15] with $[Fe_2(CN)_{10}]^{4-}$ we have found a marked cation effect with a reactivity sequence $K^+ > Na^+ > Li^+$, as illustrated by the data in Table 2. L-Ascorbic acid normally undergoes redox reactions by an outer-sphere mechanism,[8] and we attribute the cation effects to the formation of an ion triplet $[Fe_2(CN)_{10}]^{4-}\cdot M^+\cdot A^{p-}$, with the cation facilitating association of the two redox anions due to Coulombic effects. Marked cation effects are well known[1] in other reactions involving two ionic reactants. Third-order kinetics, $[A][M^+][Fe_2(CN)_{10}{}^{4-}]$ could, of course, arise from a second-order reaction between an ion pair and an anion. We have observed slight differences with NaCl, $NaNO_3$ and $NaClO_4$ but no more than might be expected for an ionic strength of 1.0 mol dm^{-3}.

Scheme 1 shows the postulated mechanism for the first stage of the reaction which leads to equations (2) and (3). As the pK_a

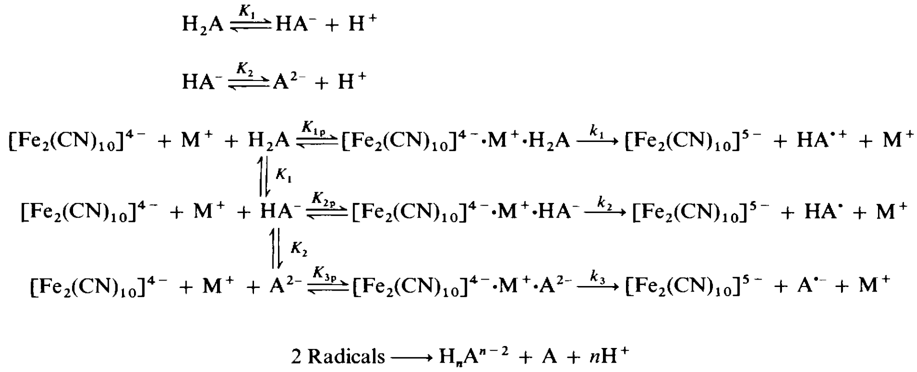
$$\text{rate} = (k_2[HA^-] + k_3[A^{2-}])[Fe_2(CN)_{10}{}^{4-}] \qquad (2)$$

$$\text{Rate} = \frac{k'_2K_1[H^+] + k''_3K_1K_2}{K_1K_2 + K_1[H^+] + [H^+]^2}\cdot[A]_T[\text{complex}] \qquad (3)$$

Table 2 Effect of alkali-metal cation on the reaction rate. [complex] = 1.7 × 10^{-4} mol dm^{-3}; [ascorbate] = 2.0 × 10^{-2} mol dm^{-3}; pH 5.33; 19.9 °C, $[MNO_3]$ = 0.98 mol dm^{-3}

	k_{obs}/s^{-1}	
Cation	First stage	Second stage
Li^+	91.3	11.0
Na^+	112 (102)*	17.6
K^+	254	61.4

* With NaCl as supporting electrolyte.



$$H_2A \underset{}{\overset{K_1}{\rightleftharpoons}} HA^- + H^+$$

$$HA^- \underset{}{\overset{K_2}{\rightleftharpoons}} A^{2-} + H^+$$

$$\begin{array}{l}
[Fe_2(CN)_{10}]^{4-} + M^+ + H_2A \overset{K_{1p}}{\rightleftharpoons} [Fe_2(CN)_{10}]^{4-}\cdot M^+\cdot H_2A \xrightarrow{k_1} [Fe_2(CN)_{10}]^{5-} + HA^{\bullet +} + M^+ \\
\qquad \Big\updownarrow K_1 \\
[Fe_2(CN)_{10}]^{4-} + M^+ + HA^- \overset{K_{2p}}{\rightleftharpoons} [Fe_2(CN)_{10}]^{4-}\cdot M^+\cdot HA^- \xrightarrow{k_2} [Fe_2(CN)_{10}]^{5-} + HA^{\bullet} + M^+ \\
\qquad \Big\updownarrow K_2 \\
[Fe_2(CN)_{10}]^{4-} + M^+ + A^{2-} \overset{K_{3p}}{\rightleftharpoons} [Fe_2(CN)_{10}]^{4-}\cdot M^+\cdot A^{2-} \xrightarrow{k_3} [Fe_2(CN)_{10}]^{5-} + A^{\bullet -} + M^+
\end{array}$$

$$2\ \text{Radicals} \longrightarrow H_nA^{n-2} + A + nH^+$$

Scheme 1 H_2A = Undissociated ascorbic acid, HA^- = monohydroascorbate anion, A^{2-} = ascorbate dianion

Table 3 Rate constants for the reaction of L-ascorbic acid with the di-µ-cyano-bis[tetracyanoferrate(III)] ion

	First stage		Second stage	
$T/°C$	$10^{-4}k'_2$/dm^3 mol^{-1} s^{-1}	$10^{-9}k''_3$/dm^3 mol^{-1} s^{-1}	$10^{-3}k'_5$/dm^3 mol^{-1} s^{-1}	$10^{-8}k''_6$/dm^3 mol^{-1} s^{-1}
19.1	0.644 ± 0.010	2.48	1.25 ± 0.01	2.98
23.6	0.887 ± 0.010	4.43	1.78 ± 0.01	3.39
27.9	1.05 ± 0.01	7.57	2.10 ± 0.02	4.91

of $HA^{\bullet}$ is −0.45 the oxidation product[8] of HA^- is written as $A^{\bullet -} + H^+$. The pseudo-second-order rate constants k'_2 and k''_3 are the products of the equilibrium constants for the ion-triplet formation and the actual rate constants k_2 and k_3 as shown in Scheme 1. The values were obtained by carrying out a least-squares analysis of the data using equation (4). These rate

$$\frac{k_{obs}(K_1K_2 + K_1[H^+] + [H^+]^2)}{[A]_T} = k'_2[H^+] + k''_3K_1K_2 \quad (4)$$

constants are shown in Table 3. For the second process we propose a mechanism similar to that in Scheme 1, with $[Fe_2(CN)_{10}]^{5-}$ as oxidant in place of $[Fe_2(CN)_{10}]^{4-}$, and with K_{5p}, K_{6p}, k_5 and k_6 in place of K_{2p}, K_{3p}, k_2 and k_3 respectively. These rate constants are also shown in Tables 1–3.

The reaction was studied only over a narrow temperature range, therefore calculating activation parameters would be of little value. Also the activation parameters would refer to rate constants that are composite quantities so that a qualitative description of any meaningful effects of those parameters is not possible.

The results in Table 3 show a very much higher reactivity for A^{2-} than for HA^-, in line with the observations of other workers. Martinez *et al.*[5] have studied the oxidation of ascorbic acid by $[Fe(CN)_6]^{3-}$, and their results can be compared to ours. For A^{2-}, they find $k = 2 \times 10^7$ dm^3 mol^{-1} s^{-1} at 25 °C while for HA^-, $k = 730$ dm^3 mol^{-1} s^{-1} both of which are lower than our value. This is reasonable in view of the higher E° value of 0.57 V for the $[Fe_2(CN)_{10}]^{4-}$–$[Fe_2(CN)_{10}]^{5-}$ couple[15] as compared to 0.36 V for $[Fe(CN)_6]^{3-}$–$[Fe(CN)_6]^{4-}$.[15] The standard reduction potential for $[Fe_2(CN)_{10}]^{5-}$–$[Fe_2(CN)_{10}]^{6-}$ is 0.36 V, and we see that our rate constants k'_5 and k''_6 are closer to the Martinez values. These E° values may be sensitive to pH and to the concentration and nature of the cations present. For oxidation by $[Fe(CN)_5(tu)]^{2-}$ (tu = thiourea) the rate constants are 8.8×10^7 and 66 dm^3 mol^{-1} s^{-1} with an E° of 0.35 V.

We had hoped to use these data to calculate self-exchange rate constants for the $Fe^{III}Fe^{III}$–$Fe^{III}Fe^{II}$ and $Fe^{III}Fe^{II}$–$Fe^{II}Fe^{II}$ couples, however the values obtained were much higher than that for $[Fe(CN)_6]^{3-}$–$[Fe(CN)_6]^{4-}$. Our rate constants incorporate effects due to the presence of the alkali-metal cation, and further work is needed to assess the possible significance of the values.

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