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Kinetic study of the oxidation of ascorbic acid by aqueous copper(II) catalysed by chloride ion*

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Two methods of monitoring the chloride-catalysed oxidation of ascorbic acid by aqueous Cu^{II} have been developed that allow the reaction conditions to be varied more widely than previously and thereby permit a fuller elucidation of the behaviour and rate law for this system. It has been possible to study the reaction over a wide concentration range from 1.6 to 500 mM Cl^- and 4 to 100 mM Cu^{II}. For the first time, it is shown that the ascorbic acid (H_2asc)–Cu^{II}–chloride ion–Cu^{I}–dehydroascorbic acid (dha) system comes to equilibrium, under anaerobic conditions, with all species present and is driven towards products by chloride complexation of Cu^{I}. The results are consistent with the following reaction scheme (i = 0–2). The full rate law has been elucidated and values for various k_{1i}, k_{-2i} and k_{2i}/k_{-1i} have been determined.

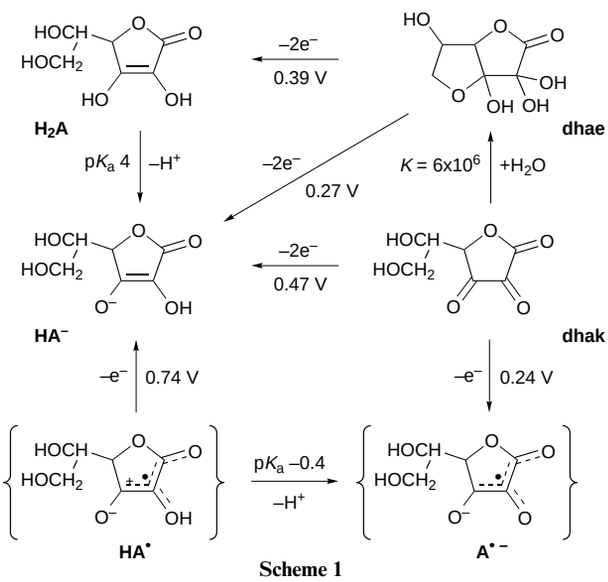
$$Hasc^- + Cu^{II}Cl_i^{+2-i} \underset{k_{-1i}}{\overset{k_{1i}}{\rightleftharpoons}} Cu^{I}Cl_i^{+1-i} + asc^{\bullet -} + H^+$$

$$asc^{\bullet -} + Cu^{II}Cl_i^{+2-i} \underset{k_{-2i}}{\overset{k_{2i}}{\rightleftharpoons}} Cu^{I}Cl_i^{+1-i} + dha$$

There have been several studies of the copper(II)–ascorbic acid system, and the earlier work has been summarized by Xu and Jordan.[1] In the latter study the dependence of the rate on chloride-ion concentration was quantified, but the mechanistic source of this catalysis was not established. The present study was undertaken to extend the results of Xu and Jordan using different monitoring methods, and to expand the experimental concentration range of the reactants in order more fully to expose the rate law with the hope that this would provide insight into the mechanism. An understanding of the mechanism should allow one to determine whether chloride-ion catalysis of oxidations by copper(II) can be expected to be a general phenomenon or is unique to ascorbic acid.

The oxidation pathways of ascorbic acid are summarized in Scheme 1, where the reduction potentials are taken from the recent summary of Tur'yan and Kohen.[2] The process involves not only an electron transfer but also cyclization finally to give bicyclic enol (dhae), commonly called dehydroascorbic acid. The enol is presumed to form by hydration of the keto intermediate (dhak). The one-electron oxidation radical ($A^{\bullet -}$) has been detected in pulse radiolysis–ESR studies,[3] but the speciation is somewhat ambiguous because of the formation of several hydroxy radical adducts and their rearrangement. However, the same dominant radical also has been produced by photosensitized oxidation of sodium ascorbate by $Ru(bpy)_3^{2+}$ (bpy = 2,2′-bipyridine) in dimethyl sulfoxide.[4] The stages at which the cyclization and hydration occur are still rather uncertain. In the ESR spectrum of $A^{\bullet -}$ the hyperfine coupling to the H at C^6 (at the end of the sidechain) is larger than to that at C^5, and this led to the suggestion[5] that the radical is cyclized. Kirino and Kwan[6] found the same coupling for the radical formed from the 5,6-isopropylidene derivative of ascorbic acid. This derivative cannot cyclize, but the 5,6-isopropylidene substituent is easily hydrolysed,[7] and the observations of Kiro and Kwan may actually pertain to ascorbic acid. Further background chemistry has been summarized by Sisley and Jordan.[8]

The reduction potentials show that the oxidation of H_2A by aqueous Cu^{II} is thermodynamically unfavourable. The auto-



Scheme 1

oxidation reaction in the presence of dioxygen is driven to products by the oxidation of Cu^{I} by O_2. Under the anaerobic conditions of the present study, chloride ion serves an analogous purpose by complexing with the Cu^{I}, but then the extent of reaction depends on the chloride-ion concentration. This gives some control of the equilibrium position and allows a more detailed kinetic characterization of the system.

Results

In the present study the oxidation of ascorbic acid by copper(II) has been followed by two monitoring techniques. In the first method the direct disappearance of Cu^{II} has been observed at 750 nm. This method is limited to concentrations of $Cu^{II} \geqslant 3 \times 10^{-3}$ M because of the low molar absorptivity of $Cu^{II}(aq)$, and to concentrations of $Cl^- \geqslant 0.03$ M to prevent precipitation of CuCl by forming $CuCl_2^-$. In the second method the disappearance of $Co(NH_3)_5(N_3)^{2+}$ due to reduction by the copper(I) product has been observed at 518 nm. Parker and

* Dedicated to Professor R. G. Wilkins on the occasion of his 70th birthday.

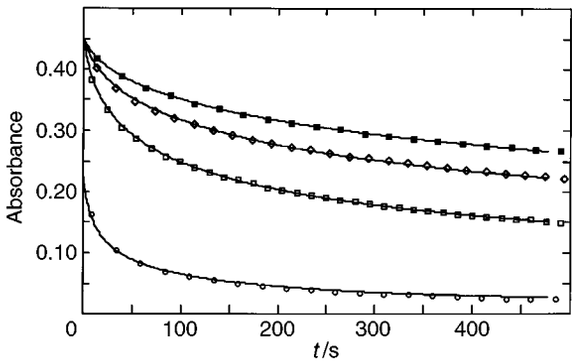


Fig. 1 Variation with time of the absorbance of Cu^{II} during reduction by ascorbic acid for runs with varying $[H^+]$; all 0.12 M Cl^- and 6.0×10^{-3} M ascorbic acid in 1.00 M $HClO_4$–$LiClO_4$ at 25 °C. The concentrations of H^+ and Cu^{II} are 0.010 and 4.01×10^{-3} (○), 0.0250 and 8.00×10^{-3} (□), 0.0502 and 8.00×10^{-3} (◇) and 0.0750 and 8.00×10^{-3} (■)

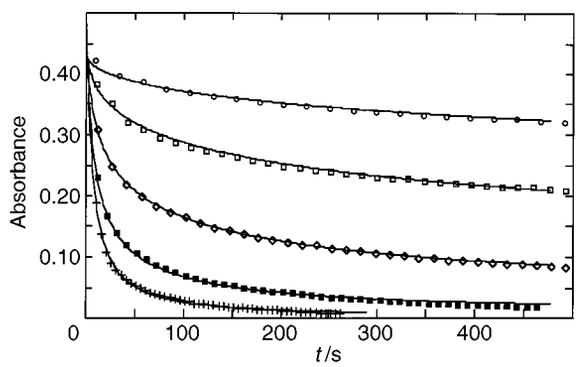


Fig. 2 Variation with time of the absorbance of Cu^{II} during reduction by ascorbic acid for runs with varying $[Cl^-]$; all 0.0100 M H^+, 8.00×10^{-3} Cu^{II} and 6.0×10^{-3} M ascorbic acid in 1.00 M $HClO_4$–$LiClO_4$ at 25 °C. The chloride concentrations are 0.0320 (○), 0.0599 (□), 0.120 (◇), 0.250 (■) and 0.500 (+)

Espenson[9] observed that the reaction $Co(NH_3)_5(N_3)^{2+}$ + $Cu^I(aq)$ is fast ($k = 1.5 \times 10^3$ M^{-1} s^{-1} at 25 °C in 0.2 M $LiClO_4$), so that $Co(NH_3)_5(N_3)^{2+}$ is an effective scavenger for $Cu^I(aq)$. The $Co(NH_3)_5(N_3)^{2+}$ has the advantage of a relatively high molar absorptivity compared to other cobalt(III) ammine complexes. This allows the study of lower copper(II) concentrations, and the low steady-state $[Cu^I]$ permits lower chloride-ion concentrations to be used.

The overall results from the two different methods of monitoring the reaction are in good agreement, but the methods differ substantially in kinetic complexity and will be discussed separately. For the conditions of this study in which the chloride-ion concentration is larger than the total copper(II, I) concentration, the overall reaction may be represented by equation (1), where H_2asc and dhae are ascorbic acid and its two-

$$H_2asc + 2\ Cu^{II} + 4\ Cl^- \longrightarrow dhae + 2\ CuCl_2^- + 2\ H^+ \quad (1)$$

electron oxidation product dehydroascorbic acid. Representation of the copper species is based on the fact that Cu^{II} is weakly complexed by Cl^-,[10] but Cu^I is strongly complexed[11–13] and is mainly present as $CuCl_2^-$. From the reduction potentials of 0.17 V for Cu^{II}–Cu^I and 0.4 V for dhae–H_2asc, it is apparent that the reaction of aqueous Cu^{II} and H_2asc is thermodynamically unfavourable. However, the overall formation constant for $CuCl_2^-$, $\beta_2^I = 1.15 \times 10^5$ M^{-2}, allows one to calculate the equilibrium constant for equation (1) as $K_1 = 2.2 \times 10^2$ M^{-2}. The reaction is exoergic and driven to the right by the complexation of Cu^I.

Direct monitoring of copper(II) disappearance

Some representative absorbance *vs.* time profiles are shown in Figs. 1–3. The majority of these profiles are unusual in that they

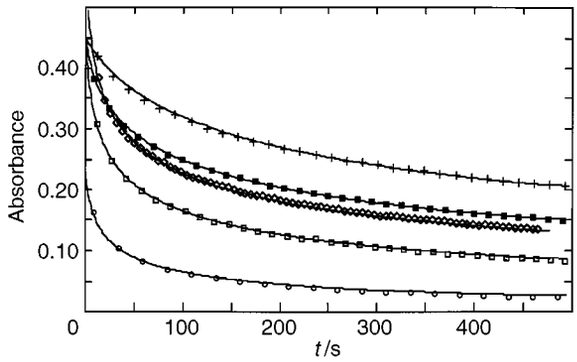


Fig. 3 Variation with time of the absorbance of Cu^{II} during reduction by ascorbic acid for runs with varying $[Cu^{II}]$ and added Cu^I; all 0.0100 M H^+ and 6.0×10^{-3} M ascorbic acid in 1.00 M $HClO_4$–$LiClO_4$ at 25 °C. The copper(II) dependence is shown for runs with 0.120 M Cl^- and the copper(II) concentrations are 4.01×10^{-3} (○), 8.00×10^{-3} (□) and 10.01×10^{-3} (◇). The copper(I) effect is shown for runs with H^+, Cl^-, and copper(II) concentrations of 0.025, 0.120 and 8.00×10^{-3} M, respectively and with initial Cu^I of 0 (■) and 4.42×10^{-3} (+)

$$H_2asc \rightleftharpoons Hasc^- + H^+; \qquad K_a = 1 \times 10^{-4}\ M$$
$$Cu^{2+} + Cl^- \rightleftharpoons Cu^{II}Cl^+; \qquad \beta_1^{II} = 2.36\ M^{-1}$$
$$Cu^{2+} + 2\ Cl^- \rightleftharpoons Cu^{II}Cl_2; \qquad \beta_2^{II} = 1.48\ M^{-2}$$
$$Cu^+ + Cl^- \rightleftharpoons Cu^ICl; \qquad \beta_1^I = 5.1 \times 10^2\ M^{-1}$$
$$Cu^+ + 2\ Cl^- \rightleftharpoons Cu^ICl_2^-; \qquad \beta_2^I = 1.15 \times 10^5\ M^{-2}$$

Scheme 2

$$Hasc^- + Cu^{II}Cl_i^{+2-i} \underset{k_{-1i}}{\overset{k_{1i}}{\rightleftharpoons}} Cu^ICl_i^{+1-i} + asc^{\bullet -} + H^+$$

$$asc^{\bullet -} + Cu^{II}Cl_i^{+2-i} \underset{k_{-2i}}{\overset{k_{2i}}{\rightleftharpoons}} Cu^ICl_i^{+1-i} + dha$$

Scheme 3

show an initial rapid absorbance change, followed by a slow almost linear change of absorbance with time. Qualitatively, Figs. 1 and 2 show that the rate decreases with increasing $[H^+]$ and increases with increasing $[Cl^-]$. The three lower curves in Fig. 3 show that the rate increases with increasing $[Cu^{II}]$, and the upper curves show that addition of Cu^I decreases the rate.

After consideration of several generic reaction schemes, it was determined that the absorbance *vs.* time profiles could be fitted if the slowing of the reaction is caused by the increasing copper(I) product concentration. Since the speciation in this system is rather well defined by previous studies, we will proceed to a general mechanism that has been found to be consistent with the observations. In developing such a scheme the species and reactions in Scheme 2 have been considered as being in rapidly maintained equilibria, with the values of β_i^{II} from Ramette[10] and of β_i^I from Arhland and Rawthorne,[11] Fritz[12] and Sharma and Millero.[13]

Then the general mechanism in Scheme 3 can be formulated, with $i = 0$, 1, 2. In Scheme 3, the anion $Hasc^-$ is shown as the reactive form of the reducing agent and this will be confirmed by the $[H^+]$ dependence of the experimental reaction rate. The product of the initial electron transfer in Scheme 3 is given as the ascorbate radical anion because the radical Hasc$^\bullet$ is a strong acid with $pK_a \approx -0.45$, based on the pulse radiolysis–ESR observations of Laroff *et al.*[3]

The rate law for Scheme 3 can be developed with a steady-state assumption for the radical $asc^{\bullet -}$. It also will be assumed at this stage that the chloride-ion concentration is in pseudo-first-order excess, a feature that is true for most but not all of these experiments. With this assumption, the concentrations of the copper species are given by equations (2) and (3), where

$$[Cu^{2+}] = \frac{[Cu^{II}]_{tot}}{D^{II}}; \quad [CuCl^{+}] = \frac{\beta_1^{II}[Cl^-][Cu^{II}]_{tot}}{D^{II}};$$

$$[CuCl_2] = \frac{\beta_2^{II}[Cl^-]^2[Cu^{II}]_{tot}}{D^{II}} \qquad (2)$$

$$[Cu^{+}] = \frac{[Cu^{I}]_{tot}}{D^{I}}; \quad [CuCl] = \frac{\beta_1^{I}[Cl^-][Cu^{I}]_{tot}}{D^{I}};$$

$$[CuCl_2^-] = \frac{\beta_2^{I}[Cl^-]^2[Cu^{I}]_{tot}}{D^{II}} \qquad (3)$$

$D^{II} = 1 + \beta_1^{II}[Cl^-] + \beta_2^{II}[Cl^-]^2$ and $D^{I} = 1 + \beta_1^{I}[Cl^-] + \beta_2^{I}[Cl^-]^2$. Then the rate of disappearance of Cu^{II} is given by equation (4),

$$\text{Rate} = -2\left\{\frac{\dfrac{k_1K_a[Cu^{II}]_{tot}^2[Hasc]_{tot}}{[H^+](D^{II})^2} - \dfrac{k_1[Cu^{I}]_{tot}^2[H^+][dha]}{K_{00}(D^{I})^2}}{\dfrac{k_1[H^+][Cu^{I}]_{tot}}{k_{-2}K_{00}D^{I}} + \dfrac{[Cu^{II}]_{tot}}{D^{II}}}\right\} \qquad (4)$$

where the rate and equilibrium constants are defined in terms of Scheme 2 as shown in equations (5)–(7), where $K_{00} = 4.1 \times 10^{-4}$ M. The first term in the denominator of equation (4) has been obtained by substitution using the relationship in equation (8). Simple rearrangement of equation (4) yields (9).

$$k_1 = k_{10} + k_{11}\beta_1^{II}[Cl^-] + k_{12}\beta_2^{II}[Cl^-]^2 \qquad (5)$$

$$k_{-2} = k_{-20} + k_{-21}\beta_1^{I}[Cl^-] + k_{-22}\beta_2^{I}[Cl^-]^2 \qquad (6)$$

$$K_{00} = \frac{[Cu^{+}]^2[H^+][dha]}{[Cu^{2+}]^2[Hasc^-]} = \frac{k_{10}k_{20}}{k_{-10}k_{-20}} \qquad (7)$$

$$k_{-1}/k_2 = k_1/k_{-2}K_{00} \qquad (8)$$

$$\frac{d[Cu^{II}]_{tot}}{dt} = -2\left\{\frac{\dfrac{k_1K_a[Cu^{II}]_{tot}^2[Hasc]_{tot}}{[H^+]D^{II}} - \dfrac{k_1D^{II}[Cu^{I}]_{tot}^2[H^+][dha]}{K_{00}(D^{I})^2}}{\dfrac{k_1D^{II}[H^+][Cu^{I}]_{tot}}{k_{-2}K_{00}D^{I}} + [Cu^{II}]_{tot}}\right\} \qquad (9)$$

Qualitatively, this rate law may be expected to fit the observations because the $[Cu^{I}]$ term in the denominator becomes larger as the reaction proceeds and will cause the rate to decrease if this term is significant relative to $[Cu^{II}]_{tot}$. It should be noted that during the more rapid initial change the rate will be substantially controlled by k_1, while during the slower, nearly linear change the rate will be controlled by k_{-2}. Since the latter region is dominant for many runs the value of k_{-2} is quite well defined.

The absorbance *vs.* time profiles were analysed by numerical integration of equation (9) because the total ascorbic acid concentration was not always in pseudo-first-order excess over the total copper(II), and free $[Cl^-]$ decreases somewhat due to complexing with Cu^{I} as predicted by Scheme 3. The overall stoichiometry and increase in $[H^+]$ predicted by equation (1) were assumed. For each run, the initial absorbance was determined from blank solutions of Cu^{II} and Cl^- at the appropriate concentrations and the variation of this with free $[Cl^-]$ during a run was taken into account. The deadtime between mixing and start of observation was treated as an adjustable parameter for each run, and was in the expected range of 10 to 15 s.

During the numerical analysis for each run k_1 was assumed to follow equation (5), and k_{10} and k_{11} were fixed at the values determined in the earlier study. In this case the numerical analysis has only two adjustable parameters, k_{12} and k_{-2}. If the assumptions are correct, then k_{12} and k_{-2} should not change as $[H^+]$ is changed in different runs, and k_{12} should be independent of $[Cl^-]$. However, k_{-2} may have a $[Cl^-]$ dependence as given by equation (6), and will actually vary during a given run because the free $[Cl^-]$ varies somewhat due to complexation with the copper(I) product.

Table 1 Kinetic results for oxidation of ascorbic acid by copper(II) while observing the disappearance of aqueous copper(II) in 1.00 M $HClO_4$–$LiClO_4$ at 25 °C

$[H^+]$/M	$[Cl^-]$/M	$10^3\,[Cu^{2+}]_{tot}$/M	$10^3\,[asc]_{tot}$/M	k_{-2}/$M^{-1}\,s^{-1}$
0.0100	0.0302	8.00	6.00	0.34
0.0100	0.0601	5.94	2.66	1.45
0.0100	0.0601	5.94	2.66	1.45
0.0100	0.0599	8.00	3.50	1.40
0.0100	0.0599	8.00	6.00	1.35
0.0100	0.1200	4.01	5.99	6.8
0.0100	0.1200	8.00	6.00	6.5
0.0100	0.1200	10.01	5.99	5.7
0.0100	0.2500	8.00	6.00	28
0.0100	0.5000	8.00	6.00	120
0.0251	0.0600	8.00	6.00	1.40
0.0250	0.1200	8.00	5.98	6.5
0.0253 *	0.120	8.00	6.00	5.5
0.0502	0.0599	8.00	3.49	1.60
0.0502	0.0599	8.00	6.00	1.55
0.0502	0.120	8.00	5.99	6.5
0.0753	0.0600	8.00	5.99	1.60
0.0750	0.120	8.00	6.01	6.5

* Contains initially $[Cu^{I}] = 4.42 \times 10^{-3}$ M

In the penultimate analysis the effect of $[Cl^-]$ variation on k_{-2} was ignored, and the apparent k_{-2} values in Table 1 were determined. These values are generally consistent with the expectation described above in that they are independent of $[H^+]$ and have a ±10% range for a particular initial $[Cl^-]$. Although not normally unusual, such a range of values is disturbing because k_{-2} is so well defined by the data and it turns out simply to be due to the $[Cl^-]$ variation. This is qualitatively apparent from Table 1, where it can be seen that smaller k_{-2} values are obtained at the higher $[Cu^{II}]_{tot}$ and $[asc]_{tot}$ values; these are runs in which more Cu^{I} is produced to complex with the Cl^-. In the final analysis it was found that k_{-2} is given by equation (10), and

$$k_{-2} = (5.1 \pm 0.1) \times 10^2\,[Cl^-]^2 \qquad (10)$$

this was included in the final numerical integration model to fit the data. Comparison to equation (6) indicates that $k_{-22}\beta_2^{I} = 5.1 \times 10^2$ M^{-3} s^{-1}, so that $k_{-22} = 4.4 \times 10^{-3}$ M^{-1} s^{-1}. There is no detectable contribution from k_{-20} or $k_{-21}\beta_1^{I}[Cl^-]$ over the range of 0.03 to 0.50 M Cl^-, and one can estimate an upper limit of $k_{-21}\beta_1^{I} < 5$ M^{-2} s^{-1}.

The value of k_1 is consistent with the earlier values of k_{10} and k_{11} except at the two highest chloride-ion concentrations, where the predicted rate is too slow. This indicates the presence of the $[Cl^-]^2$ term in equation (5) with $k_{12}\beta_2^{II} = (6.0 \pm 0.5) \times 10^3$ M^{-3} s^{-1}, so that k_1 is given by equation (11).

$$k_1 = 4.0 + 5.8 \times 10^3\,[Cl^-] + 6.0 \times 10^3\,[Cl^-]^2 \qquad (11)$$

Monitoring of $Co(NH_3)_5(N_3)^{2+}$ disappearance

The principle of this method is that the Cu^{I} produced by ascorbic acid reduction of Cu^{II} will be oxidized back to Cu^{II} by the $Co(NH_3)_5(N_3)^{2+}$. Then the system can be described by equations (12) and (13), and the disappearance of $Co(NH_3)_5$-

$$H_2asc + 2\,Cu^{II} + 2n\,Cl^- \longrightarrow dhae + 2\,CuCl_n^{1-n} + 2\,H^+ \qquad (12)$$

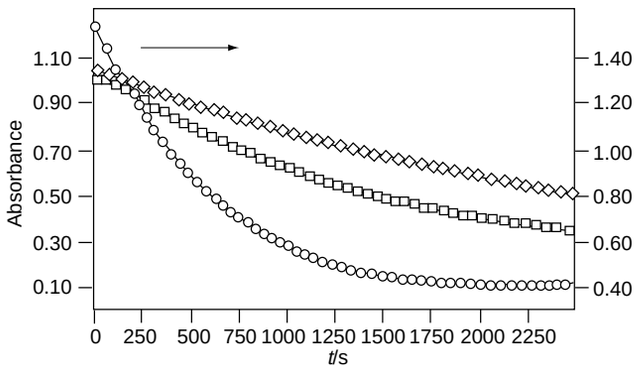


Fig. 4 Variation with time of the absorbance of $Co(NH_3)_5(N_3)^{2+}$ during reduction of Cu^{II} by ascorbic acid for runs with 0.0500 M H^+ in 1.00 M $HClO_4$–$LiClO_4$ at 25 °C. The concentrations of Cu^{II}, Cl^-, ascorbic acid and $Co(NH_3)_5(N_3)^{2+}$ respectively are 0.0501, 2.42×10^{-3}, 4.64×10^{-4}, 12.1×10^{-4} (○) offset down by 0.30 absorbance units, 0.0250, 1.604×10^{-3}, 3.48×10^{-4}, 8.02×10^{-4} (□) and 0.0126, 1.602×10^{-3}, 3.48×10^{-4}, 8.01×10^{-4} (◇)

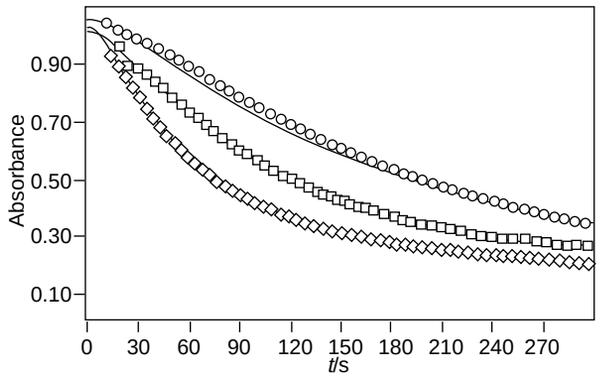


Fig. 5 Variation with time of the absorbance of $Co(NH_3)_5(N_3)^{2+}$ during reduction of Cu^{II} by ascorbic acid for runs with varying $[H^+]$ in 1.00 M $HClO_4$–$LiClO_4$ at 25 °C. The concentrations of H^+, Cu^{II}, Cl^-, ascorbic acid and $Co(NH_3)_5(N_3)^{2+}$ respectively are 0.050, 5.01×10^{-2}, 31.6×10^{-3}, 3.55×10^{-4}, 8.10×10^{-4} (○), 0.0252, 5.00×10^{-2}, 32.3×10^{-3}, 3.39×10^{-4}, 7.72×10^{-4} (□) and 0.0120, 5.00×10^{-2}, 31.5×10^{-3}, 3.46×10^{-4}, 7.85×10^{-4} (◇)

$$CuCl_n^{1-n} + Co(NH_3)_5(N_3)^{2+} + 6\,H^+ \longrightarrow Cu^{II} + nCl^- + Co^{II} + 5\,NH_4^+ + HN_3 \quad (13)$$

$(N_3)^{2+}$ can be used to monitor the Cu^{II}–ascorbic acid reaction. It was established that $Co(NH_3)_5(N_3)^{2+}$ does not react with ascorbic acid under our reaction conditions.

This method appears to provide several technical and kinetic advantages. The electronic spectrum of $Co(NH_3)_5(N_3)^{2+}$ (ε 260 M^{-1} cm^{-1} at 518 nm) makes its disappearance easy to monitor at modest concentrations. The oxidation of Cu^I [equation (13)] should maintain a low steady-state concentration of Cu^I so that the inhibition effect described in the previous section should be minimized. Substantial H^+ is consumed in equation (13), and this places some limit on the reactant concentrations if $[H^+]$ is to remain reasonably constant. The chloride-ion concentration will stay constant in a run because very little is complexed by the small amount of Cu^I. In practice, these advantages proved to be somewhat illusory for two reasons. The rate of reaction (13) is substantially inhibited by Cl^- while reaction (12) is catalysed by Cl^-. As a result, the rate of reaction (13) influences the observations, and even dominates the kinetics for $[Cl^-] \geqslant 0.04$ M. At intermediate $[Cl^-]$ the copper(I) concentration builds to small but significant levels (10^{-4}–10^{-5} M) and the copper(I) inhibition is significant. At low $[Cl^-]$ (<1×10^{-2} M) the copper(I) concentration is small (10^{-7}–10^{-8} M) because reaction (12) is slower than (13), and no copper(I) inhibition is observed. It is doubtful if the complexities of this system could have been unravelled without the knowledge gained from the direct monitoring of copper(II) disappearance.

It seems simplest to note at this stage that the rate of reaction (13) seems to be adequately described by equation (14), with

$$\text{Rate} = k_{13}[Cu^+_{aq}][Co(NH_3)_5(N_3)^{2+}] = k_{13}[Cu^I]_{tot}[Co(NH_3)_5(N_3)^{2+}]/D^I \quad (14)$$

$k_{13} = 2.6 \times 10^3$ M^{-1} s^{-1} (1.00 M $HClO_4$–$LiClO_4$), in reasonable agreement with the value of 1.5×10^3 M^{-1} s^{-1} (0.20 M $LiClO_4$) determined by Parker and Espenson.[9] The absence of $[Cl^-]$ or $[Cl^-]^2$ terms in the rate law indicates that CuCl and $CuCl_2^-$ are not kinetically active reducing agents for $Co(NH_3)_5(N_3)^{2+}$. This is not surprising because of their substantially lower reducing power compared to Cu^+(aq).

Representative absorbance *vs.* time curves are shown in Figs. 4–6. For the runs in Fig. 4 the $[Cl^-]$ is low (1.6 mM), and reaction (13) is fast enough so that k_{1i} [Scheme 3 and equation (11)] is rate controlling. In Fig. 5, the increase in rate with decreasing $[H^+]$ is shown, with other concentrations essentially constant. The variation of the rate with $[Cl^-]$ is shown in Fig. 6; these

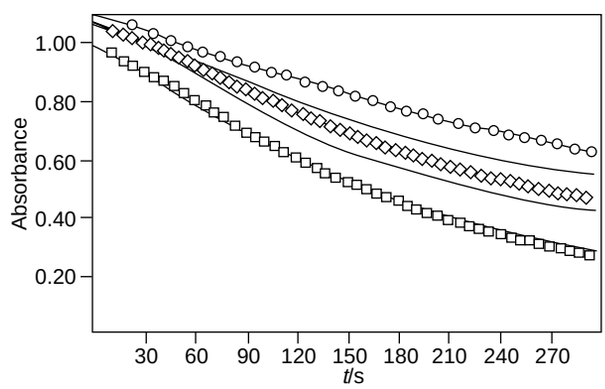


Fig. 6 Variation with time of the absorbance of $Co(NH_3)_5(N_3)^{2+}$ during reduction of Cu^{II} by ascorbic acid for runs with varying $[Cl^-]$ in 0.050 M $[H^+]$, 5.0×10^{-2} M Cu^{II} and 1.00 M $HClO_4$–$LiClO_4$ at 25 °C. The concentrations of Cl^-, ascorbic acid and $Co(NH_3)_5(N_3)^{2+}$ are 11.7×10^{-3}, 3.54×10^{-4}, 7.85×10^{-4} (○), 31.6×10^{-3}, 3.55×10^{-4}, 8.10×10^{-4} (□) and 62.2×10^{-3}, 3.51×10^{-4}, 8.02×10^{-4} (◇). The data for the upper (○) and lower (□) curves have been displaced by 0.07 absorbance units, up and down, respectively, for clarity. The three curves for the 62×10^{-3} M Cl^- data (◇) use k_{13} values of 10, 8 and 6 M s^{-1}

data illustrate the complication that arises at high $[Cl^-]$ due to the slowness of reaction (13). The rate clearly increases as $[Cl^-]$ changes from 11.7 to 31.6 mM, but then decreases at 62.2 mM. This apparent anomaly results because reaction (13) is inhibited by Cl^- and has become entirely rate limiting at 62.2 mM Cl^-. In fact the rate of reaction (13) has an influence on all the curves in Fig. 6. The run at 62.2 mM clearly shows the initial induction period due to build-up of Cu^I, and this feature is apparent but less obvious for other runs in Figs. 5 and 6.

Owing to the complexities described above, the absorbance *vs.* time profiles have been modelled by numerical integration. The stoichiometry described by reactions (12) and (13) was assumed, and the predicted change in $[H^+]$ was also taken into account. The expected ascorbic acid : $Co(NH_3)_5(N_3)^{2+}$ stoichiometry was confirmed by the observed total absorbance changes. The concentration of Cl^- stays essentially constant because of the low copper(I) concentration, but $CuCl^+$ and $CuCl_2$ formation were included in the analysis.

The numerical analysis was carried out by treating k_{-2} [equation (9)] and k_{13} [equation (14)] as fitting variables with k_1 given by equation (11). Of course, it was expected that k_{-2} would be given by equation (10), and k_{13} was adjusted accordingly to fit the absorbance *vs.* time curves. However, k_{13} is quite well estab-

Table 2 Kinetic runs for oxidation of ascorbic acid by Cu^{II} in the presence of $Co(NH_3)_5(N_3)^{2+}$ in 1.00 M $HClO_4$–$LiClO_4$ at 25 °C

$[H^+]$/M	$10^3[Cl^-]$/M	$10^2[Cu^{2+}]_{tot}$/M	$10^4[asc]_{tot}$/M	$10^4[Co(NH_3)_5(N_3)^{2+}]$/M	k_{-2}/M^{-1} s^{-1}	$10^{-2}k_{13}$/$M^{-1}s^{-1}$
0.0500	1.602	1.26	3.48	8.01		(13)*
0.0500	1.604	2.50	3.48	8.02		(13)*
0.0500	1.606	5.00	3.49	8.03		(13)*
0.0500	1.606	5.01	2.46	8.03		(13)*
0.0500	2.42	5.00	4.64	12.1		(9.9)*
0.0500	6.50	5.01	3.55	8.02		(4.0)*
0.0500	11.7	5.01	3.47	7.99	0.045	2.0
0.0500	11.7	5.00	3.54	7.85	0.048	2.2
0.0500	20.7	5.00	3.49	7.88	0.15	0.55
0.0500	31.6	5.01	3.55	8.10	0.32	0.35
0.0500	61.9	5.01	3.52	13.9	1.44	0.080
0.0500	62.2	5.01	3.47	8.02	1.40	0.080
0.0500	62.2	5.01	3.51	8.02	1.42	0.080
0.0252	32.3	5.00	3.39	7.72	0.33	0.30
0.0252	31.6	10.4	3.49	7.95	0.32	0.38
0.0252	31.1	10.4	2.18	4.99	0.35	0.30
0.0120	31.5	5.00	3.46	7.85	0.32	0.35

* Calculated from equation (14), k_1 is rate controlling under these conditions.

lished independently for runs with $[Cl^-] \geqslant 0.02$ M for reasons described above. For $[Cl^-] \leqslant 0.01$ M as in Fig. 4 k_{-2} has no influence and the rate of reduction of $Co(NH_3)_5(N_3)^{2+}$ [equation (13)] is fast enough so that the rate is controlled by k_1 [equation (9)].

The values of k_{-2} and k_{13} for different runs are given in Table 2, and representative fits for the various conditions are shown in Figs. 4–6. The values and $[Cl^-]$ dependence of k_{-2} are consistent with the results from the direct observation of copper(II) disappearance (Table 1).

Discussion

The results of this study are consistent with the earlier observations of Xu and Jordan[1] on the rate of oxidation of ascorbic acid by Cu^{II} at modest chloride-ion and copper(II) concentrations. It has been established here that the reaction is inhibited by copper(I) species, and details of the chloride-ion catalysis and reactivity patterns are elucidated by studies at higher $[Cl^-]$. All the observations can be accounted for by the reaction sequence in Scheme 3. The large effect of Cl^- on the rate results from the strong complexation of Cu^I by Cl^- and weak complexation by Cu^{II}. This gives the order of driving force for the oxidant as $Cu^{II}Cl_2 \gg Cu^{II}Cl^+ \gg Cu^{2+}$ and this is reflected in the reactivity as expected from Marcus theory for electron-transfer reactions.

The kinetically determined values of $k_{11}\beta_1^{II}$ and $k_{12}\beta_2^{II}$ [equation (5)] can be used to calculate that $k_{11} = 2.5 \times 10^3$ and $k_{12} = 4.0 \times 10^3$ M^{-1} s^{-1}. The appropriate reduction potentials and the K_a of Hasc$^\bullet$ can be used to calculate the respective equilibrium constants of $K_{11} = 5 \times 10^{-8} \times 2.5$ and $K_{12} = 1.8 \times 10^{-5} \times 2.5$. The forward rate constants and equilibrium constants can be used to calculate the reverse rate constants of $k_{-11} = 2 \times 10^{10}$ and $k_{-12} = 1 \times 10^8$ M^{-1} s^{-1}. It is not unexpected that the reverse reactions should be close to diffusion controlled, given the large driving force for the reverse reaction and that one of the reactants is a radical. Although k_{-11} seems about 5 times larger than expected for diffusion control, this could be due to uncertainty in the K_a or to a change of ≈0.03 V in the $E°$ used to calculate K_{11}.

For the purpose of the numerical analysis, it was convenient to express equation (9) with k_{-2} as a variable, but the ratios $k_{22}:k_{-11}$ and $k_{22}:k_{-12}$ are useful in providing estimates of k_{22}. From the general expression given by equation (15) it can be

$$k_{1i}k_{2j}\beta_i^{II}\beta_k^{II}/k_{-1i}k_{-2j}\beta_i^{I}\beta_k^{I} = K_{00} \qquad (15)$$

seen that the kinetically determined values of $k_{11}\beta_1^{II}$ and $k_{12}\beta_2^{II}$ [equation (5)] and $k_{-22}\beta_2^{I}$ [equation (10)] and the known values of K_{00} and βs can be used to calculate the desired ratios. The results are given by equations (16) and (17). From these ratios

$$\frac{k_{22}}{k_{-11}} = K_{00}\frac{(k_{-22}\beta_2^{I})\beta_1^{I}}{(k_{11}\beta_1^{II})\beta_2^{II}} = 0.011 \qquad (16)$$

$$\frac{k_{22}}{k_{-12}} = K_{00}\frac{(k_{-22}\beta_2^{I})\beta_2^{I}}{(k_{12}\beta_2^{II})\beta_2^{II}} = 2.3 \qquad (17)$$

and the above estimates of k_{-11} and k_{-12} one can calculate that k_{22} is 2×10^8 or 2.3×10^8 M^{-1} s^{-1} and these values are self-consistent and reasonable for reaction with a radical as discussed for k_{-11} and k_{-12}.

The values of k_{22} and $K_{22} = ([CuCl_2^-][dha]/[CuCl_2][asc^{\bullet -}])([dhae]/[dhak]) = 5.3 \times 10^3 \times 6 \times 10^6$ can be combined to calculate $k_{-22} = 0.6 \times 10^{-3}$ M^{-1} s^{-1}. This can be compared to $k_{-22} = 4.4 \times 10^{-3}$ M^{-1} s^{-1} from the experimental value of $k_{-22}\beta_2^{I} = 5.1 \times 10^2$ M^{-3} s^{-1}. The factor of 7 difference between these values can be ascribed to uncertainties in the parameters used to calculate K_{22}.

The simplified Marcus relationship is given by equation (18)

$$k_{rxn} = (k_{I/II}k_{r/p}K_{eq})^{\frac{1}{2}} \qquad (18)$$

where $k_{I/II}$ and $k_{r/p}$ are the self-exchange rate constants for the appropriate Cu^I/Cu^{II} and radical/parent reactions, respectively, and K_{eq} is the equilibrium constant for the reaction. This equation predicts that the ratio of $k_{11}:k_{12}$ can be used to estimate the ratio of $k_{I/II}(Cu^{II/I}Cl)$ to $k_{I/II}(Cu^{II/I}Cl_2)$ from the reduction potentials of the appropriate Cu^{II}–Cu^I half-reactions because the $k_{r/p}$ for ascorbate cancels when the ratio is taken. The calculation gives $k_{I/II}(Cu^{II/I}Cl):k_{I/II}(Cu^{II/I}Cl_2) = 1.4 \times 10^2:1$. The smaller value for $k_{I/II}(Cu^{II/I}Cl_2)$ could be due to a larger inner-sphere reorganization energy between the linear $Cu^ICl_2^-$ and tetragonal $CuCl_2(OH_2)_4$.

It is interesting that our studies with $Co(NH_3)_5(N_3)^{2+}$ have a formal analogy to the much studied autooxidation of ascorbic acid by Cu^{II} in which O_2 oxidizes Cu^I back to Cu^{II}. The substantial kinetic disagreements between some of the autooxidation studies have been described previously.[1] Without labouring the point, it is clear from equation (9) that the apparent order of the reaction can depend on the relative reagent concentrations and whether initial rates or the full reaction were used to determine the rate constant.

In general, the kinetic complexity of this system results because the initial electron transfer to produce the ascorbate radical is highly unfavourable and therefore subject to inhib-

ition by the copper(I) product. Similar effects can be expected for many organic reductants that give unstable radical intermediates. The chloride-ion catalysis results in large part from the strong complexation of Cu^{I} by chloride ion which increases K_{eq} in equation (18) and thereby increases the rate constant. It appears that any species that complexes with Cu^{I} much more strongly than with Cu^{II} should have an analogous catalytic effect, as long as the self-exchange rate $k_{I/II}$ is not proportionately decreased.

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