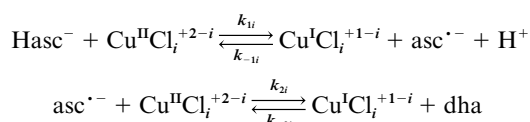


# Kinetic study of the oxidation of ascorbic acid by aqueous copper(II) catalysed by chloride ion\*

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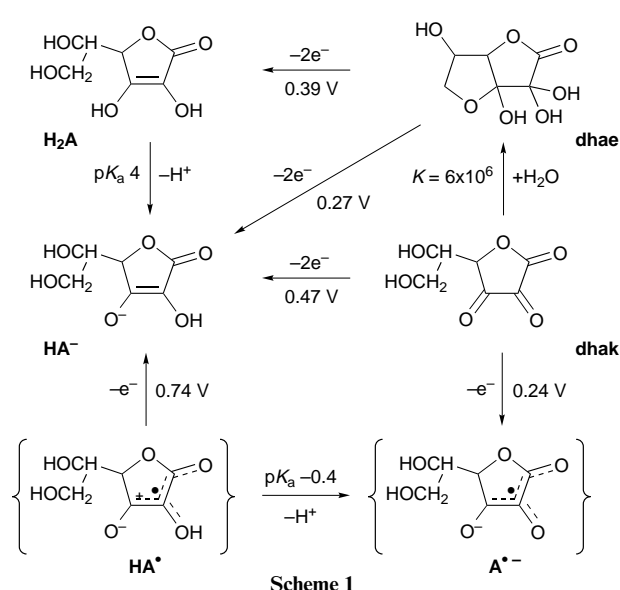
Two methods of monitoring the chloride-catalysed oxidation of ascorbic acid by aqueous  $\text{Cu}^{\text{II}}$  have been developed that allow the reaction conditions to be varied more widely than previously and thereby permit a fuller elucidation of the behaviour and rate law for this system. It has been possible to study the reaction over a wide concentration range from 1.6 to 500 mM  $\text{Cl}^-$  and 4 to 100 mM  $\text{Cu}^{\text{II}}$ . For the first time, it is shown that the ascorbic acid ( $\text{H}_2\text{A}$ )– $\text{Cu}^{\text{II}}$ –chloride ion– $\text{Cu}^{\text{I}}$ –dehydroascorbic acid (dha) system comes to equilibrium, under anaerobic conditions, with all species present and is driven towards products by chloride complexation of  $\text{Cu}^{\text{I}}$ . 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.



There have been several studies of the copper(II)–ascorbic acid system, and the earlier work has been summarized by Xu and Jordan.<sup>1</sup> 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.<sup>2</sup> 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 ( $\text{A}^{\cdot-}$ ) has been detected in pulse radiolysis–ESR studies,<sup>3</sup> 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  $\text{Ru}(\text{bpy})_3^{2+}$  ( $\text{bpy} = 2,2'$ -bipyridine) in dimethyl sulfoxide.<sup>4</sup> The stages at which the cyclization and hydration occur are still rather uncertain. In the ESR spectrum of  $\text{A}^{\cdot-}$  the hyperfine coupling to the H at  $\text{C}^6$  (at the end of the sidechain) is larger than to that at  $\text{C}^5$ , and this led to the suggestion<sup>5</sup> that the radical is cyclized. Kirino and Kwan<sup>6</sup> 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,<sup>7</sup> and the observations of Kiro and Kwan may actually pertain to ascorbic acid. Further background chemistry has been summarized by Sisley and Jordan.<sup>8</sup>

The reduction potentials show that the oxidation of  $\text{H}_2\text{A}$  by aqueous  $\text{Cu}^{\text{II}}$  is thermodynamically unfavourable. The auto-

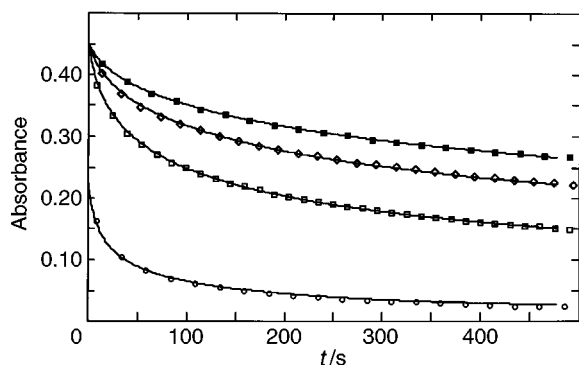


oxidation reaction in the presence of dioxygen is driven to products by the oxidation of  $\text{Cu}^{\text{I}}$  by  $\text{O}_2$ . Under the anaerobic conditions of the present study, chloride ion serves an analogous purpose by complexing with the  $\text{Cu}^{\text{I}}$ , but then the extent of reaction depends on the chloride-ion concentration. This gives some control of the equilibrium position and allows a more detailed kinetic characterization of the system.

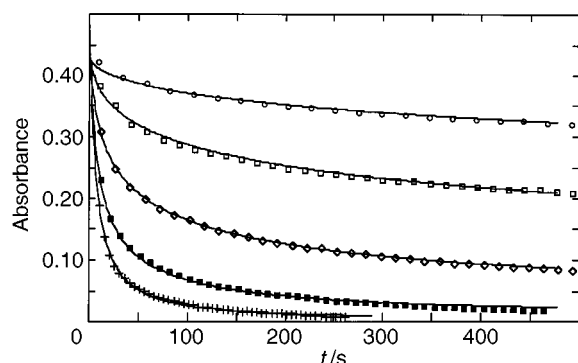
## Results

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  $\text{Cu}^{\text{II}}$  has been observed at 750 nm. This method is limited to concentrations of  $\text{Cu}^{\text{II}} \geq 3 \times 10^{-3}$  M because of the low molar absorptivity of  $\text{Cu}^{\text{II}}(\text{aq})$ , and to concentrations of  $\text{Cl}^- \geq 0.03$  M to prevent precipitation of  $\text{CuCl}$  by forming  $\text{CuCl}_2^-$ . In the second method the disappearance of  $\text{Co}(\text{NH}_3)_5(\text{N}_3)^{2+}$  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.



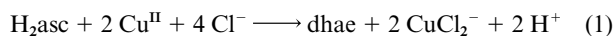
**Fig. 1** Variation with time of the absorbance of  $\text{Cu}^{\text{II}}$  during reduction by ascorbic acid for runs with varying  $[\text{H}^+]$ ; all  $0.12 \text{ M Cl}^-$  and  $6.0 \times 10^{-3} \text{ M}$  ascorbic acid in  $1.00 \text{ M HClO}_4\text{--LiClO}_4$  at  $25^\circ\text{C}$ . The concentrations of  $\text{H}^+$  and  $\text{Cu}^{\text{II}}$  are  $0.010$  and  $4.01 \times 10^{-3}$  ( $\circ$ ),  $0.0250$  and  $8.00 \times 10^{-3}$  ( $\square$ ),  $0.0502$  and  $8.00 \times 10^{-3}$  ( $\diamond$ ) and  $0.0750$  and  $8.00 \times 10^{-3}$  ( $\blacksquare$ )



**Fig. 2** Variation with time of the absorbance of  $\text{Cu}^{\text{II}}$  during reduction by ascorbic acid for runs with varying  $[\text{Cl}^-]$ ; all  $0.0100 \text{ M H}^+$ ,  $8.00 \times 10^{-3} \text{ M Cu}^{\text{II}}$  and  $6.0 \times 10^{-3} \text{ M}$  ascorbic acid in  $1.00 \text{ M HClO}_4\text{--LiClO}_4$  at  $25^\circ\text{C}$ . The chloride concentrations are  $0.0320$  ( $\circ$ ),  $0.0599$  ( $\square$ ),  $0.120$  ( $\diamond$ ),  $0.250$  ( $\blacksquare$ ) and  $0.500$  ( $+$ )

Espenson<sup>9</sup> observed that the reaction  $\text{Co}(\text{NH}_3)_5(\text{N}_3)^{2+} + \text{Cu}^{\text{I}}(\text{aq})$  is fast ( $k = 1.5 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$  at  $25^\circ\text{C}$  in  $0.2 \text{ M LiClO}_4$ ), so that  $\text{Co}(\text{NH}_3)_5(\text{N}_3)^{2+}$  is an effective scavenger for  $\text{Cu}^{\text{I}}(\text{aq})$ . The  $\text{Co}(\text{NH}_3)_5(\text{N}_3)^{2+}$  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  $[\text{Cu}^{\text{I}}]$  permits lower chloride-ion concentrations to be used.

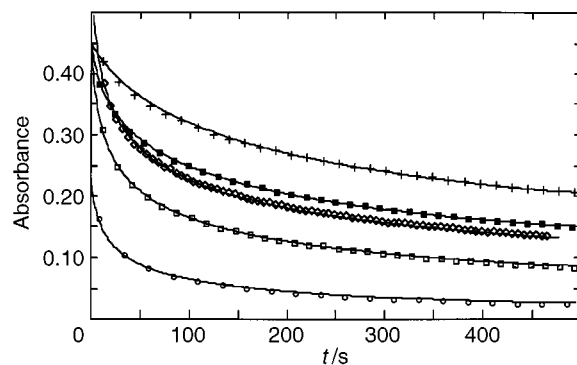
The overall results from the two different methods of monitoring the reaction are in good agreement, but the methods differ substantially in kinetic complexity and will be discussed separately. For the conditions of this study in which the chloride-ion concentration is larger than the total copper(II, I) concentration, the overall reaction may be represented by equation (1), where  $\text{H}_2\text{asc}$  and  $\text{dhae}$  are ascorbic acid and its two-



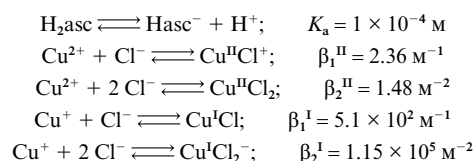
electron oxidation product dehydroascorbic acid. Representation of the copper species is based on the fact that  $\text{Cu}^{\text{II}}$  is weakly complexed by  $\text{Cl}^-$ ,<sup>10</sup> but  $\text{Cu}^{\text{I}}$  is strongly complexed<sup>11–13</sup> and is mainly present as  $\text{CuCl}_2^-$ . From the reduction potentials of  $0.17 \text{ V}$  for  $\text{Cu}^{\text{II}}\text{--Cu}^{\text{I}}$  and  $0.4 \text{ V}$  for  $\text{dhae}\text{--H}_2\text{asc}$ , it is apparent that the reaction of aqueous  $\text{Cu}^{\text{II}}$  and  $\text{H}_2\text{asc}$  is thermodynamically unfavourable. However, the overall formation constant for  $\text{CuCl}_2^-$ ,  $\beta_2^{\text{I}} = 1.15 \times 10^5 \text{ M}^{-2}$ , allows one to calculate the equilibrium constant for equation (1) as  $K_1 = 2.2 \times 10^2 \text{ M}^{-2}$ . The reaction is exoergic and driven to the right by the complexation of  $\text{Cu}^{\text{I}}$ .

#### Direct monitoring of copper(II) disappearance

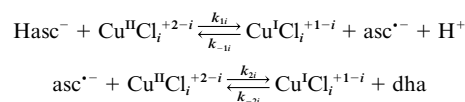
Some representative absorbance vs. time profiles are shown in Figs. 1–3. The majority of these profiles are unusual in that they



**Fig. 3** Variation with time of the absorbance of  $\text{Cu}^{\text{II}}$  during reduction by ascorbic acid for runs with varying  $[\text{Cu}^{\text{II}}]$  and added  $\text{Cu}^{\text{I}}$ ; all  $0.0100 \text{ M H}^+$  and  $6.0 \times 10^{-3} \text{ M}$  ascorbic acid in  $1.00 \text{ M HClO}_4\text{--LiClO}_4$  at  $25^\circ\text{C}$ . The copper(II) dependence is shown for runs with  $0.120 \text{ M Cl}^-$  and the copper(II) concentrations are  $4.01 \times 10^{-3}$  ( $\circ$ ),  $8.00 \times 10^{-3}$  ( $\square$ ) and  $10.01 \times 10^{-3}$  ( $\diamond$ ). The copper(I) effect is shown for runs with  $\text{H}^+$ ,  $\text{Cl}^-$ , and copper(II) concentrations of  $0.025$ ,  $0.120$  and  $8.00 \times 10^{-3} \text{ M}$ , respectively and with initial  $\text{Cu}^{\text{I}}$  of  $0$  ( $\blacksquare$ ) and  $4.42 \times 10^{-3}$  ( $+$ )



#### Scheme 2



#### 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  $[\text{H}^+]$  and increases with increasing  $[\text{Cl}^-]$ . The three lower curves in Fig. 3 show that the rate increases with increasing  $[\text{Cu}^{\text{II}}]$ , and the upper curves show that addition of  $\text{Cu}^{\text{I}}$  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  $\beta_i^{\text{II}}$  from Ramette<sup>10</sup> and of  $\beta_i^{\text{I}}$  from Arhland and Rawthorne,<sup>11</sup> Fritz<sup>12</sup> and Sharma and Millero.<sup>13</sup>

Then the general mechanism in Scheme 3 can be formulated, with  $i = 0, 1, 2$ . In Scheme 3, the anion  $\text{Hasc}^-$  is shown as the reactive form of the reducing agent and this will be confirmed by the  $[\text{H}^+]$  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  $\text{Hasc}^{\cdot-}$  is a strong acid with  $\text{p}K_a \approx -0.45$ , based on the pulse radiolysis–ESR observations of Laroff *et al.*<sup>3</sup>

The rate law for Scheme 3 can be developed with a steady-state assumption for the radical  $\text{asc}^{\cdot-}$ . 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

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

$$[\text{CuCl}_2] = \frac{\beta_2^{\text{II}}[\text{Cl}^-]^2[\text{Cu}^{\text{II}}]_{\text{tot}}}{D^{\text{II}}} \quad (2)$$

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

$$[\text{CuCl}_2^-] = \frac{\beta_2^{\text{I}}[\text{Cl}^-]^2[\text{Cu}^{\text{I}}]_{\text{tot}}}{D^{\text{I}}} \quad (3)$$

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

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

$$\frac{k_1 [\text{H}^+][\text{Cu}^{\text{I}}]_{\text{tot}}}{k_{-2} K_{00} D^{\text{I}}} + \frac{[\text{Cu}^{\text{II}}]_{\text{tot}}}{D^{\text{II}}}$$

where the rate and equilibrium constants are defined in terms of Scheme 2 as shown in equations (5)–(7), where  $K_{00} =$

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

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

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

$4.1 \times 10^{-4}$  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).

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

$$\frac{d[\text{Cu}^{\text{II}}]_{\text{tot}}}{dt} = -2 \left\{ \frac{k_1 K_a [\text{Cu}^{\text{II}}]_{\text{tot}}^2 [\text{Hasc}]_{\text{tot}} - k_1 D^{\text{II}} [\text{Cu}^{\text{I}}]_{\text{tot}}^2 [\text{H}^+][\text{dha}]}{[\text{H}^+]D^{\text{II}} - K_{00}(D^{\text{I}})^2} \right\} \quad (9)$$

$$\frac{k_1 D^{\text{II}} [\text{H}^+][\text{Cu}^{\text{I}}]_{\text{tot}}}{k_{-2} K_{00} D^{\text{I}}} + [\text{Cu}^{\text{II}}]_{\text{tot}}$$

Qualitatively, this rate law may be expected to fit the observations because the  $[\text{Cu}^{\text{I}}]$  term in the denominator becomes larger as the reaction proceeds and will cause the rate to decrease if this term is significant relative to  $[\text{Cu}^{\text{II}}]_{\text{tot}}$ . 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  $[\text{Cl}^-]$  decreases somewhat due to complexing with  $\text{Cu}^{\text{I}}$  as predicted by Scheme 3. The overall stoichiometry and increase in  $[\text{H}^+]$  predicted by equation (1) were assumed. For each run, the initial absorbance was determined from blank solutions of  $\text{Cu}^{\text{II}}$  and  $\text{Cl}^-$  at the appropriate concentrations and the variation of this with free  $[\text{Cl}^-]$  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

**Table 1** Kinetic results for oxidation of ascorbic acid by copper(II) while observing the disappearance of aqueous copper(II) in 1.00 M  $\text{HClO}_4$ – $\text{LiClO}_4$  at 25 °C

$[\text{H}^+]/\text{M}$	$[\text{Cl}^-]/\text{M}$	$10^3 [\text{Cu}^{2+}]_{\text{tot}}/\text{M}$	$10^3 [\text{asc}]_{\text{tot}}/\text{M}$	$k_{-2}/\text{M}^{-1} \text{s}^{-1}$
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  $[\text{Cu}^{\text{I}}] = 4.42 \times 10^{-3}$  M

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  $[\text{H}^+]$  is changed in different runs, and  $k_{12}$  should be independent of  $[\text{Cl}^-]$ . However,  $k_{-2}$  may have a  $[\text{Cl}^-]$  dependence as given by equation (6), and will actually vary during a given run because the free  $[\text{Cl}^-]$  varies somewhat due to complexation with the copper(I) product.

In the penultimate analysis the effect of  $[\text{Cl}^-]$  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  $[\text{H}^+]$  and have a  $\pm 10\%$  range for a particular initial  $[\text{Cl}^-]$ . 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  $[\text{Cl}^-]$  variation. This is qualitatively apparent from Table 1, where it can be seen that smaller  $k_{-2}$  values are obtained at the higher  $[\text{Cu}^{\text{II}}]_{\text{tot}}$  and  $[\text{asc}]_{\text{tot}}$  values; these are runs in which more  $\text{Cu}^{\text{I}}$  is produced to complex with the  $\text{Cl}^-$ . In the final analysis it was found that  $k_{-2}$  is given by equation (10), and

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

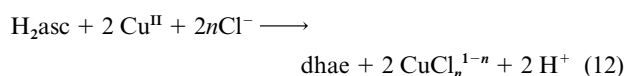
this was included in the final numerical integration model to fit the data. Comparison to equation (6) indicates that  $k_{-22}\beta_2^{\text{I}} = 5.1 \times 10^2 \text{ M}^{-3} \text{s}^{-1}$ , so that  $k_{-22} = 4.4 \times 10^{-3} \text{ M}^{-1} \text{s}^{-1}$ . There is no detectable contribution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

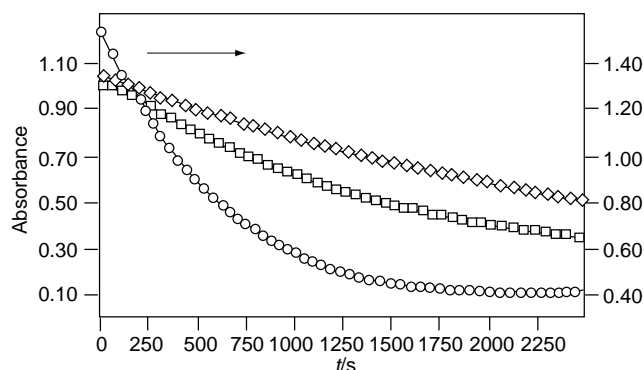
The value of  $k_1$  is consistent with the earlier values of  $k_{10}$  and  $k_{11}$  except at the two highest chloride-ion concentrations, where the predicted rate is too slow. This indicates the presence of the  $[\text{Cl}^-]^2$  term in equation (5) with  $k_{12}\beta_2^{\text{II}} = (6.0 \pm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

$$k_1 = 4.0 + 5.8 \times 10^3 [\text{Cl}^-] + 6.0 \times 10^3 [\text{Cl}^-]^2 \quad (11)$$

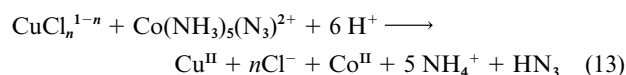
### Monitoring of $\text{Co}(\text{NH}_3)_5(\text{N}_3)^{2+}$ disappearance

The principle of this method is that the  $\text{Cu}^{\text{I}}$  produced by ascorbic acid reduction of  $\text{Cu}^{\text{II}}$  will be oxidized back to  $\text{Cu}^{\text{II}}$  by the  $\text{Co}(\text{NH}_3)_5(\text{N}_3)^{2+}$ . Then the system can be described by equations (12) and (13), and the disappearance of  $\text{Co}(\text{NH}_3)_5$





**Fig. 4** Variation with time of the absorbance of  $\text{Co}(\text{NH}_3)_5(\text{N}_3)^{2+}$  during reduction of  $\text{Cu}^{\text{II}}$  by ascorbic acid for runs with  $0.0500 \text{ M H}^+$  in  $1.00 \text{ M HClO}_4\text{--LiClO}_4$  at  $25^\circ\text{C}$ . The concentrations of  $\text{Cu}^{\text{II}}$ ,  $\text{Cl}^-$ , ascorbic acid and  $\text{Co}(\text{NH}_3)_5(\text{N}_3)^{2+}$  respectively are  $0.0501$ ,  $2.42 \times 10^{-3}$ ,  $4.64 \times 10^{-4}$ ,  $12.1 \times 10^{-4}$  ( $\circ$ ) offset down by  $0.30$  absorbance units,  $0.0250$ ,  $1.604 \times 10^{-3}$ ,  $3.48 \times 10^{-4}$ ,  $8.02 \times 10^{-4}$  ( $\square$ ) and  $0.0126$ ,  $1.602 \times 10^{-3}$ ,  $3.48 \times 10^{-4}$ ,  $8.01 \times 10^{-4}$  ( $\diamond$ )



$(\text{N}_3)^{2+}$  can be used to monitor the  $\text{Cu}^{\text{II}}$ –ascorbic acid reaction. It was established that  $\text{Co}(\text{NH}_3)_5(\text{N}_3)^{2+}$  does not react with ascorbic acid under our reaction conditions.

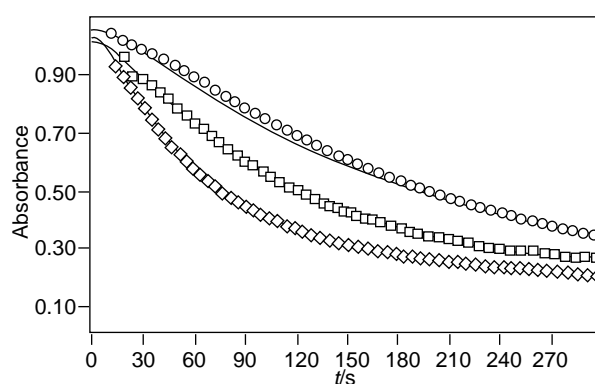
This method appears to provide several technical and kinetic advantages. The electronic spectrum of  $\text{Co}(\text{NH}_3)_5(\text{N}_3)^{2+}$  ( $\epsilon$   $260 \text{ M}^{-1} \text{ cm}^{-1}$  at  $518 \text{ nm}$ ) makes its disappearance easy to monitor at modest concentrations. The oxidation of  $\text{Cu}^{\text{I}}$  [equation (13)] should maintain a low steady-state concentration of  $\text{Cu}^{\text{I}}$  so that the inhibition effect described in the previous section should be minimized. Substantial  $\text{H}^+$  is consumed in equation (13), and this places some limit on the reactant concentrations if  $[\text{H}^+]$  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  $\text{Cu}^{\text{I}}$ . In practice, these advantages proved to be somewhat illusory for two reasons. The rate of reaction (13) is substantially inhibited by  $\text{Cl}^-$  while reaction (12) is catalysed by  $\text{Cl}^-$ . As a result, the rate of reaction (13) influences the observations, and even dominates the kinetics for  $[\text{Cl}^-] \geq 0.04 \text{ M}$ . At intermediate  $[\text{Cl}^-]$  the copper(I) concentration builds to small but significant levels ( $10^{-4}$ – $10^{-5} \text{ M}$ ) and the copper(I) inhibition is significant. At low  $[\text{Cl}^-]$  ( $< 1 \times 10^{-2} \text{ M}$ ) the copper(I) concentration is small ( $10^{-7}$ – $10^{-8} \text{ M}$ ) 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

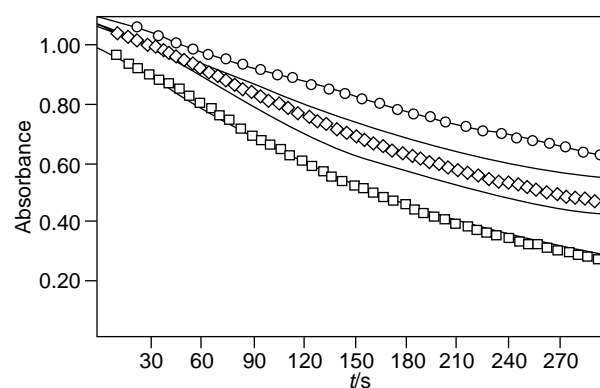
$$\text{Rate} = k_{13}[\text{Cu}^+_{\text{aq}}][\text{Co}(\text{NH}_3)_5(\text{N}_3)^{2+}] = k_{13}[\text{Cu}^+]_{\text{tot}}[\text{Co}(\text{NH}_3)_5(\text{N}_3)^{2+}]/D^{\text{I}} \quad (14)$$

$k_{13} = 2.6 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$  ( $1.00 \text{ M HClO}_4\text{--LiClO}_4$ ), in reasonable agreement with the value of  $1.5 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$  ( $0.20 \text{ M LiClO}_4$ ) determined by Parker and Espenson.<sup>9</sup> The absence of  $[\text{Cl}^-]$  or  $[\text{Cl}^-]^2$  terms in the rate law indicates that  $\text{CuCl}$  and  $\text{CuCl}_2^-$  are not kinetically active reducing agents for  $\text{Co}(\text{NH}_3)_5(\text{N}_3)^{2+}$ . This is not surprising because of their substantially lower reducing power compared to  $\text{Cu}^+(\text{aq})$ .

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



**Fig. 5** Variation with time of the absorbance of  $\text{Co}(\text{NH}_3)_5(\text{N}_3)^{2+}$  during reduction of  $\text{Cu}^{\text{II}}$  by ascorbic acid for runs with varying  $[\text{H}^+]$  in  $1.00 \text{ M HClO}_4\text{--LiClO}_4$  at  $25^\circ\text{C}$ . The concentrations of  $\text{H}^+$ ,  $\text{Cu}^{\text{II}}$ ,  $\text{Cl}^-$ , ascorbic acid and  $\text{Co}(\text{NH}_3)_5(\text{N}_3)^{2+}$  respectively are  $0.050$ ,  $5.01 \times 10^{-2}$ ,  $31.6 \times 10^{-3}$ ,  $3.55 \times 10^{-4}$ ,  $8.10 \times 10^{-4}$  ( $\circ$ ),  $0.0252$ ,  $5.00 \times 10^{-2}$ ,  $32.3 \times 10^{-3}$ ,  $3.39 \times 10^{-4}$ ,  $7.72 \times 10^{-4}$  ( $\square$ ) and  $0.0120$ ,  $5.00 \times 10^{-2}$ ,  $31.5 \times 10^{-3}$ ,  $3.46 \times 10^{-4}$ ,  $7.85 \times 10^{-4}$  ( $\diamond$ )



**Fig. 6** Variation with time of the absorbance of  $\text{Co}(\text{NH}_3)_5(\text{N}_3)^{2+}$  during reduction of  $\text{Cu}^{\text{II}}$  by ascorbic acid for runs with varying  $[\text{Cl}^-]$  in  $0.050 \text{ M H}^+$ ,  $5.0 \times 10^{-2} \text{ M Cu}^{\text{II}}$  and  $1.00 \text{ M HClO}_4\text{--LiClO}_4$  at  $25^\circ\text{C}$ . The concentrations of  $\text{Cl}^-$ , ascorbic acid and  $\text{Co}(\text{NH}_3)_5(\text{N}_3)^{2+}$  are  $11.7 \times 10^{-3}$ ,  $3.54 \times 10^{-4}$ ,  $7.85 \times 10^{-4}$  ( $\circ$ ),  $31.6 \times 10^{-3}$ ,  $3.55 \times 10^{-4}$ ,  $8.10 \times 10^{-4}$  ( $\square$ ) and  $62.2 \times 10^{-3}$ ,  $3.51 \times 10^{-4}$ ,  $8.02 \times 10^{-4}$  ( $\diamond$ ). The data for the upper ( $\circ$ ) and lower ( $\square$ ) curves have been displaced by  $0.07$  absorbance units, up and down, respectively, for clarity. The three curves for the  $62 \times 10^{-3} \text{ M Cl}^-$  data ( $\diamond$ ) use  $k_{13}$  values of  $10$ ,  $8$  and  $6 \text{ M}^{-1} \text{ s}^{-1}$

data illustrate the complication that arises at high  $[\text{Cl}^-]$  due to the slowness of reaction (13). The rate clearly increases as  $[\text{Cl}^-]$  changes from  $11.7$  to  $31.6 \text{ mM}$ , but then decreases at  $62.2 \text{ mM}$ . This apparent anomaly results because reaction (13) is inhibited by  $\text{Cl}^-$  and has become entirely rate limiting at  $62.2 \text{ mM Cl}^-$ . In fact the rate of reaction (13) has an influence on all the curves in Fig. 6. The run at  $62.2 \text{ mM}$  clearly shows the initial induction period due to build-up of  $\text{Cu}^{\text{I}}$ , 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  $[\text{H}^+]$  was also taken into account. The expected ascorbic acid: $\text{Co}(\text{NH}_3)_5(\text{N}_3)^{2+}$  stoichiometry was confirmed by the observed total absorbance changes. The concentration of  $\text{Cl}^-$  stays essentially constant because of the low copper(I) concentration, but  $\text{CuCl}^+$  and  $\text{CuCl}_2^-$  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<sup>II</sup> in the presence of Co(NH<sub>3</sub>)<sub>5</sub>(N<sub>3</sub>)<sup>2+</sup> in 1.00 M HClO<sub>4</sub>–LiClO<sub>4</sub> at 25 °C

[H <sup>+</sup> ]/M	10 <sup>3</sup> [Cl <sup>−</sup> ]/M	10 <sup>2</sup> [Cu <sup>2+</sup> ] <sub>tot</sub> /M	10 <sup>4</sup> [asc] <sub>tot</sub> /M	10 <sup>4</sup> [Co(NH <sub>3</sub> ) <sub>5</sub> (N <sub>3</sub> ) <sup>2+</sup> ]/M	<i>k</i> <sub>−2</sub> /M <sup>−1</sup> s <sup>−1</sup>	10 <sup>−2</sup> <i>k</i> <sub>13</sub> /M <sup>−1</sup> s <sup>−1</sup>
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*<sub>1</sub> is rate controlling under these conditions.

lished independently for runs with [Cl<sup>−</sup>] ≥ 0.02 M for reasons described above. For [Cl<sup>−</sup>] ≤ 0.01 M as in Fig. 4 *k*<sub>−2</sub> has no influence and the rate of reduction of Co(NH<sub>3</sub>)<sub>5</sub>(N<sub>3</sub>)<sup>2+</sup> [equation (13)] is fast enough so that the rate is controlled by *k*<sub>1</sub> [equation (9)].

The values of *k*<sub>−2</sub> and *k*<sub>13</sub> 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<sup>−</sup>] dependence of *k*<sub>−2</sub> 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<sup>1</sup> on the rate of oxidation of ascorbic acid by Cu<sup>II</sup> 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<sup>−</sup>]. All the observations can be accounted for by the reaction sequence in Scheme 3. The large effect of Cl<sup>−</sup> on the rate results from the strong complexation of Cu<sup>I</sup> by Cl<sup>−</sup> and weak complexation by Cu<sup>II</sup>. This gives the order of driving force for the oxidant as Cu<sup>II</sup>Cl<sub>2</sub> ≫ Cu<sup>II</sup>Cl<sup>+</sup> ≫ Cu<sup>2+</sup> and this is reflected in the reactivity as expected from Marcus theory for electron-transfer reactions.

The kinetically determined values of *k*<sub>11</sub>β<sub>1</sub><sup>II</sup> and *k*<sub>12</sub>β<sub>2</sub><sup>II</sup> [equation (5)] can be used to calculate that *k*<sub>11</sub> = 2.5 × 10<sup>3</sup> and *k*<sub>12</sub> = 4.0 × 10<sup>3</sup> M<sup>−1</sup> s<sup>−1</sup>. The appropriate reduction potentials and the *K*<sub>a</sub> of Hasc<sup>•</sup> can be used to calculate the respective equilibrium constants of *K*<sub>11</sub> = 5 × 10<sup>−8</sup> × 2.5 and *K*<sub>12</sub> = 1.8 × 10<sup>−5</sup> × 2.5. The forward rate constants and equilibrium constants can be used to calculate the reverse rate constants of *k*<sub>−11</sub> = 2 × 10<sup>10</sup> and *k*<sub>−12</sub> = 1 × 10<sup>8</sup> M<sup>−1</sup> s<sup>−1</sup>. 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*<sub>11</sub> seems about 5 times larger than expected for diffusion control, this could be due to uncertainty in the *K*<sub>a</sub> or to a change of ≈0.03 V in the *E*<sup>o</sup> used to calculate *K*<sub>11</sub>.

For the purpose of the numerical analysis, it was convenient to express equation (9) with *k*<sub>−2</sub> as a variable, but the ratios *k*<sub>22</sub>:*k*<sub>−11</sub> and *k*<sub>22</sub>:*k*<sub>−12</sub> are useful in providing estimates of *k*<sub>22</sub>. From the general expression given by equation (15) it can be

$$k_1 k_2 \beta_1^{\text{II}} \beta_k^{\text{II}} / k_{-1} k_{-2} \beta_1^{\text{I}} \beta_k^{\text{I}} = K_{00} \quad (15)$$

seen that the kinetically determined values of *k*<sub>11</sub>β<sub>1</sub><sup>II</sup> and *k*<sub>12</sub>β<sub>2</sub><sup>II</sup> [equation (5)] and *k*<sub>−22</sub>β<sub>2</sub><sup>I</sup> [equation (10)] and the known values

of *K*<sub>00</sub> and β<sub>s</sub> can be used to calculate the desired ratios. The results are given by equations (16) and (17). From these ratios

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

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

and the above estimates of *k*<sub>−11</sub> and *k*<sub>−12</sub> one can calculate that *k*<sub>22</sub> is 2 × 10<sup>8</sup> or 2.3 × 10<sup>8</sup> M<sup>−1</sup> s<sup>−1</sup> and these values are self-consistent and reasonable for reaction with a radical as discussed for *k*<sub>−11</sub> and *k*<sub>−12</sub>.

The values of *k*<sub>22</sub> and *K*<sub>22</sub> = ([CuCl<sub>2</sub>][dha]/[CuCl<sub>2</sub>][asc<sup>•</sup>])([dhae]/[dhak]) = 5.3 × 10<sup>3</sup> × 6 × 10<sup>6</sup> can be combined to calculate *k*<sub>−22</sub> = 0.6 × 10<sup>−3</sup> M<sup>−1</sup> s<sup>−1</sup>. This can be compared to *k*<sub>−22</sub> = 4.4 × 10<sup>−3</sup> M<sup>−1</sup> s<sup>−1</sup> from the experimental value of *k*<sub>−22</sub>β<sub>2</sub><sup>I</sup> = 5.1 × 10<sup>2</sup> M<sup>−3</sup> s<sup>−1</sup>. The factor of 7 difference between these values can be ascribed to uncertainties in the parameters used to calculate *K*<sub>22</sub>.

The simplified Marcus relationship is given by equation (18)

$$k_{\text{rxn}} = (k_{\text{int}} k_{\text{rtp}} K_{\text{eq}})^{\frac{1}{2}} \quad (18)$$

where *k*<sub>int</sub> and *k*<sub>rtp</sub> are the self-exchange rate constants for the appropriate Cu<sup>I</sup>/Cu<sup>II</sup> and radical/parent reactions, respectively, and *K*<sub>eq</sub> is the equilibrium constant for the reaction. This equation predicts that the ratio of *k*<sub>11</sub>:*k*<sub>12</sub> can be used to estimate the ratio of *k*<sub>int</sub>(Cu<sup>III</sup>Cl) to *k*<sub>int</sub>(Cu<sup>III</sup>Cl<sub>2</sub>) from the reduction potentials of the appropriate Cu<sup>II</sup>–Cu<sup>I</sup> half-reactions because the *k*<sub>rtp</sub> for ascorbate cancels when the ratio is taken. The calculation gives *k*<sub>int</sub>(Cu<sup>III</sup>Cl):*k*<sub>int</sub>(Cu<sup>III</sup>Cl<sub>2</sub>) = 1.4 × 10<sup>2</sup>:1. The smaller value for *k*<sub>int</sub>(Cu<sup>III</sup>Cl<sub>2</sub>) could be due to a larger inner-sphere reorganization energy between the linear Cu<sup>I</sup>Cl<sub>2</sub><sup>−</sup> and tetragonal CuCl<sub>2</sub>(OH<sub>2</sub>)<sub>4</sub>.

It is interesting that our studies with Co(NH<sub>3</sub>)<sub>5</sub>(N<sub>3</sub>)<sup>2+</sup> have a formal analogy to the much studied autooxidation of ascorbic acid by Cu<sup>II</sup> in which O<sub>2</sub> oxidizes Cu<sup>I</sup> back to Cu<sup>II</sup>. The substantial kinetic disagreements between some of the autooxidation studies have been described previously.<sup>1</sup> 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  $\text{Cu}^{\text{I}}$  by chloride ion which increases  $K_{\text{eq}}$  in equation (18) and thereby increases the rate constant. It appears that any species that complexes with  $\text{Cu}^{\text{I}}$  much more strongly than with  $\text{Cu}^{\text{II}}$  should have an analogous catalytic effect, as long as the self-exchange rate  $k_{\text{III}}$  is not proportionately decreased.

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