for the remainder of the cluster structure. On the other hand, if the 2-coordinate boron has only one endo hydrogen attached, the adjacent B–B edges will normally be bridged, which gives what may be considered a chelating BH_4 group. Second, a 3-coordinate boron atom on the open face of the core cluster may or may not have an endo hydrogen attached, but never more than one. If a 3-coordinate boron does have an endo hydrogen, the adjacent B–B edges will not be bridged, and the boron will appear in the cluster simply as a BH_2 group. Finally, no boron atom with coordination number greater than 3 can have an endo hydrogen attached.

These generalizations on the occurrence of endo hydrogens are obviously related to the fact that EHMO calculations will tend to pile up negative charge on atoms of low coordination number. For a given skeletal geometry, skeletal MO's with increasing numbers of nodes will be most stable (hence below the HOMO and occupied) if those nodes pass near, but not through, a low-coordinate skeletal atom, because the low electron density that a node implies is no handicap if it does not occur between the two nuclei. The low-coordinate boron atom will thus be disproportionately represented in the occupied skeletal orbitals and will accumulate a high overall electron density and negative charge.

It is somewhat more difficult to offer generalizations about bridging hydrogen location. From the observed structures, it does seem clear that BHB bridges will usually involve a 3-coordinate boron atom. In particular, a bond around the open face between a 3-coordinate and a 4-coordinate boron atom will be bridged unless the presence of an endo hydrogen on the 3-coordinate boron prevents it. B–B bonds between two 4-coordinate boron atoms will be bridged only if there are no sites involving lower coordination numbers. Given the highly idealized geometric basis of our calculations, these generalizations seem to have essentially a topological origin in the nuclearity and symmetry of the core cluster, but we cannot adduce direct electronic reasons for our calculations.

In summary, the pattern of extended Hückel MO calculations presented in this series of papers is capable of predicting the occurrence of endo-terminal-hydrogen atoms in borane clusters and the number and location of both endo- and bridging-hydrogen atoms, given only the skeletal electron count and the geometric isomer of the core cluster (which can itself be predicted by these calculations). Although generalizations about these locations are possible, they do not reduce to rules as straightforward as the skeletal-electron-counting rules that have become central to cluster chemistry.

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Contribution from the Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada T6G 2G2

Kinetics and Mechanism of the Reaction of Aqueous Copper(II) with Ascorbic Acid

Jinhuang Xu and R. B. Jordan*

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The oxidation of ascorbic acid by aqueous copper(II) has been studied under anaerobic conditions with $[Cu^{2+}]$ in the range (1–5) $\times 10^{-3}$ M, total ascorbic acid concentration of 5×10^{-5} M, and $[H^+]$ of (0.50–10) $\times 10^{-3}$ M in 1.0 M $NaClO_4/HClO_4$ at 25 °C. The kinetic effect of the chloride ion concentration in the range (0.5–7) $\times 10^{-3}$ M also has been investigated. The observed pseudo-first-order rate constant is given by $k_{obsd} = (a + b[Cl^-])[Cu^{2+}]/(K_a + [H^+])$ with $a = (4.0 \pm 0.13) \times 10^{-4}$ s^{-1} and $b = 0.58 \pm 0.036$ M^{-1} s^{-1}. The results are discussed in terms of the probable mechanisms for the direct and chloride-catalyzed paths for the oxidation, and earlier results in the presence of acetate are reanalyzed.

Introduction

It has been known for many years that copper(II) oxidizes ascorbic acid under anaerobic conditions and catalyzes the oxidation of ascorbic acid by dioxygen. Most studies have concentrated on the copper(II)-catalyzed reaction with dioxygen and have paid limited attention to the direct copper(II)–ascorbic acid reaction although the latter may be an important initiation step and is an ever present background reaction.

The information on the rate law for the copper(II)-catalyzed reaction seems to be in some disarray. Khan and Martell[1,2] found the rate to be first order in $[O_2]$ and $[Cu^{2+}]$ with a pH dependence which indicated that both ascorbic acid (H_2A) and its conjugate base (HA^-) are kinetically active. The same dependence on $[O_2]$ had been found earlier by Barron et al.[3] and by Weissberger and co-workers.[4] Dekker and Dickinson[5] found an inverse second-order dependence on $[H^+]$. More recently, Jameson and Blackburn[6] found the rate law given by eq 1 with $k_r = 0.19$ (25 °C,

$$\text{rate} = k_r \frac{[Cu^{2+}][AH_2][O_2]^{0.5}}{[H^+]} \quad (1)$$

0.1 M KNO_3) and the results of Shtamm et al.[7] are in good agreement with $k_r = 0.13$ (25 °C, low ionic strength) although different chain mechanisms have been proposed to explain the results. The obvious difference between the latter two studies and that of Khan and Martell[1] seems to be that the total ascorbic acid concentration was larger than $[Cu^{2+}]$ in the latest studies.[6,7] In addition, Khan and Martell followed dehydroascorbic acid production, while Shtamm et al.[8] and Jameson and Blackburn[6] followed dioxygen loss and Shtamm and co-workers[7] also studied initial rates of Cu^+ formation. It should be noted that Jameson and Blackburn[9] have found a half-order dependence on ascorbic acid in 0.10 M KCl.

Information on the direct reaction is not in a great deal better state. Shtamm et al.[7] have concluded, by extrapolation of the $[O_2]$ dependence data used to establish eq 1, that the direct reaction is insignificant relative to the Cu(II)-catalyzed O_2 reaction.

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However, Martinez et al.[10] have reported kinetics for the direct reaction with the rate law given by eq 2. In studies of the

$$\text{rate} = 0.55\frac{[Cu^{2+}][AH_2]}{[H^+]} \quad (2)$$

catalyzed reaction with O_2, the $[O_2]$ is typically $\leq 1 \times 10^{-3}$ M so that a comparison of eqs 1 and 2 leads one to believe that the reaction is actually faster in the absence of O_2. But Martinez and co-workers studied the reaction in 1 M HCl/KCl and seem to have been unaware of earlier work,[5,11,12] which indicated that the reaction is catalyzed by the chloride ion. Therefore the above comparison is not valid because of a crucial difference in the conditions.

Hayakawa et al.[13] studied the direct reaction in 0.1 M acetate buffers (pH 4.8–5.5) with $[Cu^{2+}] \approx$ total ascorbic acid by measuring the initial rates of ascorbic acid disappearance at 265 nm. The interpretation of this study is complicated by the fact that the Cu^{2+} is essentially completely converted to $Cu(OAc)^+$ with increasing amounts of $Cu(OAc)_2$ as the pH increases.[14] Hayakawa et al. interpreted their results in terms of a rate law with terms second order in and independent of $[Cu^{2+}]$ with oxidation of HA^- and A^{2-}. However, we find that their data are not inconsistent with a first-order dependence on $[Cu^{2+}]$, and the influence of acetate complexing is discussed more fully in the following section.

Shtamm et al.[7] briefly studied the direct reaction by monitoring the initial rate of Cu^+ formation with total ascorbic acid $\gg [Cu^{2+}]$ and claim that the reaction is second order in $[Cu^{2+}]$ with the rate given by eq 3. This, compared to eq 1, predicts that the rate of

$$\text{rate} = 1.8\frac{[Cu^{2+}]^2[AH_2]}{[H^+]} \quad (3)$$

the direct reaction will be greater than that of the copper(II)-catalyzed O_2 reaction for the relatively modest conditions of $[Cu^{2+}] > 3 \times 10^{-3}$ M if $[O_2] \leq 1 \times 10^{-3}$ M. However there is an obvious discrepancy in the $[Cu^{2+}]$ dependence between the rate laws in eqs 2 and 3.

The present study was undertaken to clarify the situation with regard to the direct reaction, and with the hope of casting some light on the reaction mechanism. The reaction has been studied anaerobically in 1 M $NaClO_4/HClO_4$ under conditions of $[Cu^{2+}] \gg$ [ascorbic acid]. The latter conditions were chosen to avoid higher copper(II)–ascorbate complexes and to minimize the possible reaction of ascorbate with its oxidation product. The latter was suggested as a complication by Weissberger et al.[4] The effect of the chloride ion concentration on the rate also has been investigated under the same conditions with $[Cl^-]$ in the same range as $[Cu^{2+}]$.

Results and Discussion

The rate of disappearance of ascorbic acid was monitored at 245 nm, which is an absorbance maximum under our acidity conditions. The rate was studied as a function of the concentrations of copper(II) ($(1.0–5.0) \times 10^{-3}$ M), hydrogen ion ($(0.50–10) \times 10^{-3}$ M), and chloride ion ($(0.50–7.0) \times 10^{-3}$ M) at 25 °C in 1.0 M $NaClO_4/HClO_4$, and the results are summarized in Table I. The data indicate a first-order dependence on $[Cu^{2+}]$, an inverse first-order dependence on $[H^+]$, and a path first order in $[Cl^-]$. If the $[H^+]^{-1}$ effect is due to reaction of the conjugate base of ascorbic acid ($K_a = 9.0 \times 10^{-5}$ M[6]), then the results can be described by eq 4. A least-squares analysis gives

$$k_{obsd} = (a + b[Cl^-])\frac{[Cu^{2+}]}{K_a + [H^+]} \quad (4)$$

Table I. Kinetic Results for the Reaction of Aqueous Copper(II) with Ascorbic Acid[a]

$10^3[Cu^{2+}]$, M	$10^3[H^+]$, M	$10^3[Cl^-]$, M	10^3k_{obsd}, s^{-1}	10^3k_{calc},[c] s^{-1}
1.00	0.500	0	0.708	0.677
2.00	0.500	0	1.59	1.35
3.00	0.500	0	2.02	2.03
4.00	0.500	0	2.65	2.71
5.00	0.500	0	3.46	3.39
1.00	0.700	0	0.536	0.506
2.00	0.700	0	1.03	1.01
3.00	0.700	0	1.46	1.52
4.00	0.700	0	2.01	2.02
5.00	0.700	0	2.51	2.53
1.00	1.00	0	0.374	0.366
2.00	1.00	0	0.654	0.733
3.00	1.00	0	1.01	1.10
4.00	1.00	0	1.29	1.47
5.00	1.00	0	1.66	1.83
1.00	2.00	0	0.202	0.191
2.00	2.00	0	0.417	0.382
3.00	2.00	0	0.578	0.573
4.00	2.00	0	0.739	0.764
5.00	2.00	0	0.929	0.956
1.00	10.0	0	0.0429	0.0396
2.00	10.0	0	0.0793	0.0792
3.00	10.0	0	0.129	0.119
4.00	10.0	0	0.169	0.158
5.00	10.0	0	0.207	0.198
3.00	1.00	0	1.01	1.10
3.00	1.00	0.500	1.92	1.90
3.00	1.00	1.00	2.81	2.70
3.00	1.00	2.00	4.34	4.30
3.00	1.00	3.00	5.79	5.90
3.00	1.00	4.00	7.27	7.50
3.00	1.00	5.00	8.55	9.10
3.00	1.00	7.00	12.1	12.3
3.00	1.00	1.00	2.81	2.70
3.00	1.00	1.00	3.36[b]	2.70
3.00	1.00	3.00	5.86	5.90
3.00	1.00	3.00	5.78[b]	5.90
3.00	1.00	5.00	8.99	9.10
3.00	1.00	5.00	9.15[b]	9.10

[a] All data at 25 °C in 1 M $NaClO_4/HClO_4$ with a total ascorbic acid concentration of 5.0×10^{-5} M. [b] Solutions contain equal concentrations of acetonitrile and chloride ion. [c] Values calculated from a least-squares fit to eq 4.

$a = (4.00 \pm 0.13) \times 10^{-4}$ and $b = 0.58 \pm 0.036$. The values predicted by eq 4 are compared to the experimental results in Table I.

If we disregard the chloride ion dependent path for the moment, then the simplest reaction sequence consistent with eq 4 is given in Scheme I. It is assumed that the radical intermediate $\{AH^\bullet\}$ is a strong acid, as indicated by the results of Laroff et al.,[15] although this is not necessary from the present kinetic data. It is meant to be implied in Scheme I that the k_1 path involves outer-sphere electron transfer and the k_2 path is an intramolecular process followed by rapid dissociation of the acidic $AH^\bullet$ from Cu^+.

Scheme I

$$AH_2 \overset{K_a}{\rightleftharpoons} AH^- + H^+$$

$$Cu^{2+} + AH^- \overset{K_f}{\rightleftharpoons} Cu(AH)^+$$

$$Cu^{2+} + AH^- \xrightarrow{k_1} Cu^+ + \{AH^\bullet\}$$

$$Cu(AH)^+ \xrightarrow{k_2} Cu^+ + \{AH^\bullet\}$$

$$\{AH^\bullet\} \rightleftharpoons \{A^\bullet\}^- + H^+$$

$$Cu^{2+} + \{A^\bullet\}^- \xrightarrow{\text{fast}} Cu^+ + A$$

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If it is assumed that K_a and K_f represent rapidly established equilibria, then the theoretical pseudo-first-order rate constant for Scheme I is given by eq 5. This expression will reduce to the

$$k_{obsd} = \left(\frac{k_1 K_a + k_2 K_f K_a}{[H^+] + K_a + K_f K_a [Cu^{2+}]} \right) [Cu^{2+}] \qquad (5)$$

experimental form (eq 4 with $[Cl^-] = 0$) if $[H^+] \gg K_f K_a [Cu^{2+}]$. In their study of the O_2–Cu^{2+}–ascorbate system, Jameson and Blackburn[6] used kinetic and potentiometric results to obtain $K_f K_a = 0.02$ (0.1 M KNO_3). A similar value of 0.029 (0.4 M $LiClO_4$) has been obtained by Ghosh and Gould[16] from the kinetics of a Cu^{2+}-catalyzed oxidation of ascorbate in acetate buffers, although no account is taken of acetate complexing by Cu^{2+}.[14] The values of $K_f K_a$ indicate that the condition $[H^+] \gg K_f K_a [Cu^{2+}]$ is reasonably satisfied for our conditions of $[Cu^{2+}] \leq 5 \times 10^{-3}$ M and $[H^+] \geq 0.5 \times 10^{-3}$ M.

Previous studies on ascorbate oxidations, as summarized by Macartney and Sutin,[17] indicate that H_2A is about 10^4 times less reactive than HA^- with outer-sphere reagents. Therefore it is normal that the reduction of H_2A is not observed under our acidity conditions.

It is clear from eq 5 that the kinetic observations do not allow us to differentiate between the k_1 and k_2 paths unless one or the other leads to unreasonable specific rate constants. If the outer-sphere path (k_1) dominates, it is possible to calculate that the aqueous Cu^{2+}/Cu^+ self-exchange rate must be $\sim 2 \times 10^5$ M^{-1} s^{-1} in order to predict the observed value of $k_1 = 4.4$ M^{-1} s^{-1} from the Marcus cross relation.[18] There are no measured values for this self-exchange rate, but Davies[19] has estimated a value of 1.9×10^{-4} M^{-1} s^{-1} from the Cu^+ reductions of several Ru(III) complexes. The problems with such estimates for Cu^{2+}/Cu^+ systems have been discussed recently by Rorabacher et al.[20] The latter authors found that $Co(Me_4[14]tetraeneN_4)^{3+}$ is reduced by an inner-sphere mechanism with Cu^+ and estimated the rate constant for the reverse oxidation by Cu^{2+} to be 5.2×10^{-3} M^{-1} s^{-1}. This value can be taken as an upper limit on the outer-sphere rate constant and used to calculate an upper limit of 2×10^{-3} M^{-1} s^{-1} for the Cu^{2+}/Cu^+ self-exchange rate constant. Therefore, the available evidence indicates that the value of 2×10^5 M^{-1} s^{-1} required for outer-sphere ascorbate oxidation is about 10^8 times larger than expected. It seems reasonable to conclude that the Cu^{2+}–ascorbate reaction is not proceeding by an outer-sphere mechanism.

An intramolecular mechanism (k_2) does not pose a problem for this system because the lability of aqueous Cu^{2+} allows the rapid formation of an inner-sphere complex, as shown in Scheme I. In this case, one can use the value of $K_f K_a$[6] to estimate that $k_2 \approx 4 \times 10^{-4}/0.02 = 2 \times 10^{-2}$ s^{-1}.

The mechanisms described thus far involve one-electron-transfer steps. However, copper(II) is a potential two-electron donor and one could have a two-electron-transfer process to give copper(0) as shown by the first step in eq 6. The Cu(0) could react with

$$Cu^{2+} + HA^- \rightarrow Cu + A + H^+$$
$$Cu^{2+} + Cu \rightleftarrows 2Cu^+ \qquad (6)$$

aqueous Cu^{2+} to produce Cu^+, as shown in the second step. The equilibrium constant of $\sim 10^{-6}$ M for the second step is unfavorable, and our typical Cu^{2+} concentrations of $\sim 3 \times 10^{-3}$ M give an equilibrium concentration of Cu^+ of 5.5×10^{-5} M, which would leave 4.5×10^{-5} M Cu(0) from 5×10^{-5} M ascorbic acid. Such an amount of colloidal Cu(0) would be expected to affect our spectrophotometric observations at 245 nm, but no such problems were observed.[21]

Chloride ion concentration has a remarkable effect on the reaction rate. The rate constant (b in eq 4) for the chloride-dependent path is almost 10^3 times larger than that for the chloride-independent path. The results of Martinez et al.[10] in 1.0 M KCl give a value of $b = 0.47$ in good agreement with our value of 0.58 in 1.0 M $NaClO_4$. This implies that there is relatively little saturation effect of the chloride ion concentration between 7×10^{-3} and 1.0 M. The simplest reaction sequence to rationalize the chloride ion dependence is shown in Scheme II. This involves formation of a copper(II)–chloride–ascorbate complex followed by oxidation, as in Scheme I.

Scheme II

$$AH_2 \overset{K_a}{\rightleftharpoons} AH^- + H^+$$
$$Cu^{2+} + Cl^- \overset{K_{Cl}}{\rightleftharpoons} CuCl^+$$
$$CuCl^+ + AH^- \overset{K_{f2}}{\rightleftharpoons} Cu(Cl)(AH)$$
$$Cu(Cl)(AH) \xrightarrow{k_3} CuCl + \{AH^\bullet\}$$
$$CuCl^+ + AH^- \xrightarrow{k_4} CuCl + \{AH^\bullet\}$$
$$\{AH^\bullet\} \rightleftarrows \{A^\bullet\}^- + H^+$$
$$Cu^{2+} + \{A^\bullet\}^- \xrightarrow{fast} Cu^+ + A$$

The order of the steps leading to Cu(Cl)(AH) is immaterial to the kinetic analysis, and only one possibility has been shown in Scheme II. It is also possible that this is an outer-sphere complex or ion pair[22] that would be better represented as $[Cu(Cl)^{\bullet+}(AH^-)]$. The strong catalysis by Cl^- implies that the chloride ion has a significant perturbing influence on the metal ion so that Cl^- is most probably the inner-sphere ligand, as indicated in Scheme II. There is also the possibility of an outer-sphere path involving $CuCl^+$, as represented by the k_4 path in Scheme II.

The pseudo-first order rate constant predicted by Scheme II is given by eq 7. In order to reduce eq 7 to the observed form of the second term in eq 4, it is necessary to assume that $[H^+] \gg K_f K_a$, as before, and $[H^+] \gg K_{Cl} K_{f2} K_a [Cu^{2+}][Cl^-]$. There is

$$k_{obsd} = \frac{(k_4 K_{Cl} K_a + k_3 K_{Cl} K_{f2} K_a)[Cu^{2+}][Cl^-]}{[H^+] + K_a + K_f K_a [Cu^{2+}] + K_{Cl} K_{f2} K_a [Cu^{2+}][Cl^-]} \qquad (7)$$

some disagreement about the value of K_{Cl}, except that it is small,[23,24] and the most recent analysis of Ramette[24] gives $K_{Cl} = 2.3$ M^{-1}. It seems reasonable that $K_{f2} K_a < K_f K_a$ (Scheme I), so that $K_{f2} K_a \leq 0.02$ and the last term in the denominator of eq 7 is $\sim 10^{-6}$ M at the highest $[Cu^{2+}]$ and $[Cl^-]$ of our study. Therefore, the condition that $[H^+] \gg K_{Cl} K_{f2} K_a [Cu^{2+}][Cl^-]$ is easily satisfied and eq 7 will simplify to the experimentally observed form.

Mechanistically, the electron-transfer steps in Scheme II can be viewed as either intramolecular (k_3) or outer-sphere (k_4), while the ion-pair possibility (which is not shown) is equivalent to outer-sphere with a moderately stable precursor complex. Again, the rate law does not distinguish these possibilities, so that all one can do is see if any paths can be eliminated because they give unreasonable rate constants.

If one assumes that the k_3 is dominant, then $k_3 K_{Cl} K_{f2} K_a = 0.58$ and one can estimate that $k_3 > 0.58/(2.3 \times 0.02) = 13$ s^{-1}. For the ion-pair option, K_{f2} is replaced by the ion-pair formation constant (K_i) in the previous calculation. Since K_i is likely to be in the range of 0.1 M^{-1}, this path gives a rate constant k_{3i} of ~ 3

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$\times 10^4$ s^{-1}. If k_4 is dominant, then $k_4K_{Cl}K_a = 0.58$ and $k_4 = 2.8 \times 10^2$ M^{-1} s^{-1}.

The above analysis indicates that $k_3 \geq 600k_2$ or $k_4 \approx 1.4 \times 10^4 k_2$. For either case, it seems surprising that complexation of copper(II) by chloride ion would increase the willingness of copper(II) to give up an electron. It would be easy to offer rationalizations if chloride ion were an inhibitor of the reaction.

For the outer-sphere reaction (k_4), one can calculate that the driving force for the $CuCl^+/CuCl$ couple[25] is about 0.15 V more favorable than that for the Cu^{2+}/Cu^+ couple and this would make k_4 about 14 times larger than k_2, assuming the square-root dependence of k on the equilibrium constant, as predicted by the Marcus cross relationship.[18] In addition, the self-exchange rate of the chloro complexes may be larger and this could similarly enhance the rate predicted for an outer-sphere process. A self-exchange rate constant of $\sim 2 \times 10^4$ M^{-1} s^{-1} is required to predict the observe value of k_4. McConnell and Weaver[26] measured a self-exchange rate of 5×10^7 M^{-1} s^{-1} for $CuCl_2^-/CuCl_4^{2-}$, but it is not known if the lower chloride complexes will show a proportional acceleration in the self-exchange rate.

In order to determine if the kinetic effect of chloride ion concentration might be due to the greater thermodynamic driving force, we have examined the effect of acetonitrile on the rate. It is known that CH_3CN complexes weakly with aqueous Cu^{2+} and rather strongly with Cu^+. Therefore CH_3CN is analogous to Cl^- in this regard. It should be noted that Shtamm et al.[7] have observed an accelerating effect of CH_3CN complexation in the range 0.01–0.05 M. Equilibrium constants[24] indicate that Cu^+ is about 90% in the form $Cu(NCCH_3)_2^+$ under these conditions, and Shtamm et al. found the rate to be first order in $[CH_3CN]$. The overall second formation constants (β_2) for the chloro[25,27] and acetonitrile[28] complexes are 1.1×10^5 and 2.2×10^4 M^{-1}, respectively. We have done parallel experiments in which CH_3CN was added to chloride-containing solutions at concentrations in the range $(1.0–5.0) \times 10^{-3}$ M and detect no kinetic effect of CH_3CN in the presence of chloride ions. These results are given as the last six entries in Table I.

The results of Hayakawa et al.[13] in acetate buffers are potentially relevant to the kinetic effects of complexation on the Cu^{2+} oxidation of ascorbate. These authors were aware of this possibility but did not include it in their interpretation. They also concluded that the reaction was second order in $[Cu^{2+}]$ after "correcting" the experimental rate constants for a metal ion independent factor, which they assigned to the reaction of residual dioxygen. However, the latter reaction is much too slow to contribute on the stopped-flow time scale and dioxygen would react by the copper(II)-catalyzed path in any case. We have reexamined the data tabulated by Hayakawa et al. and believe that the experimental rate constants are reasonably consistent with a first-order dependence on $[Cu^{2+}]$. We have reanalyzed the results by analogy to Scheme II, including acetate complexing ($K_{1OAc} = 51.3$ M^{-1}, $K_{2OAc} = 10$ M^{-1}),[14] and the possibility that the mixed complex $(Cu(OAc)(AH))$ ionizes to $Cu(OAc)(A)^-$ (K_a'') in the pH range 4.8–5.5. Then the $[Cu^{2+}]$ and pH dependence of the observations are reasonably predicted if the rate-controlling steps are given by eqs 8 and 9. In Figure 1, the experimental data of Hayakawa

$$Cu(OAc)(AH) \xrightarrow{k_5} Cu(OAc) + \{AH^\bullet\} \quad (8)$$

$$Cu(OAc)(A)^- \xrightarrow{k_5'} Cu(OAc) + \{A^\bullet\}^- \quad (9)$$

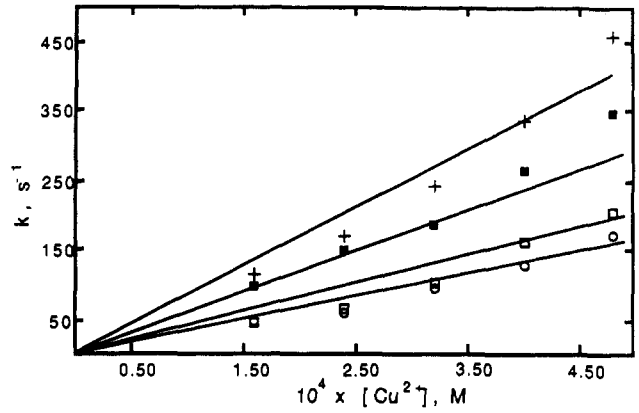

Figure 1. Data of Hayakawa et al.[13] on the variation of the rate constant for the oxidation of ascorbic acid by copper(II) in 0.1 M acetate buffers at 30 °C for pH 4.8 (○), pH 4.96 (□), pH 5.25 (■), and pH 5.5 (+). The lines are best fits to a model based on Scheme II, as described in the text.

et al. are compared to least-squares best fit lines based on this model. It is our impression that this model gives an adequate representation of the data and has the advantage of not requiring the assumption of any metal ion independent contribution. Our analysis gives $k_5K_{f2} = (3.1 \pm 0.9) \times 10^4$ M^{-1} s^{-1} and $k_5'K_{f2}K_a'' = 0.21 \pm 0.05$ s^{-1}, where K_{f2} is as defined in Scheme II except that acetate replaces chloride. It seems reasonable that $K_{f2} < K_{1OAc}$, so that $k_5 \geq 6 \times 10^2$ s^{-1}, which may be compared to the Cl^- system value of $k_3 \geq 13$ s^{-1}. The acetate system can be interpreted equally in terms of reactions such as $Cu(OAc)^+ + HA^-$ for which $k_6 = 3.1 \times 10^4$ M^{-1} s^{-1}, compared to $k_4 = 2.8 \times 10^2$ M^{-1} s^{-1} for Cl^-. Whichever interpretation is used, it appears that acetate is 50–100 times more effective than chloride at catalyzing the oxidation of ascorbate by copper(II).

The above analysis indicates that the strong rate acceleration caused by both chloride and acetate can be interpreted in terms of similar reaction schemes. The simplest conclusion would seem to be that the anions are reducing the barrier to transform Cu^{2+} into Cu^+ and this translates into a rate accleration.

Experimental Section

Materials. Solutions of copper(II) were prepared by dissolving $Cu(NO_3)_2$ in appropriate solutions of $HClO_4/NaClO_4$. The copper(II) concentration was determined by iodometric titration. Fresh solutions of ascorbic acid (Kodak, White Label) were prepared daily. Dioxygen was removed from the reaction solutions by bubbling argon for 2 h through solutions protected by serum caps. Residual dioxygen in the argon was removed by passing the argon through scrubbers containing aqueous chromium(II) perchlorate, and the dioxygen in the reaction solutions was determined to be $<10^{-6}$ M. All solutions were prepared in deionized water and then distilled from alkaline permanganate in an all-glass apparatus.

Kinetic Measurements. After solutions of copper(II) in aqueous $HClO_4/NaClO_4$ were placed in a 20 mm path length quartz cell, sealed with a serum cap, they were deoxygenated as described above. The solution was brought to 25 °C during the deoxygenation, and finally, the ascorbic acid was added by using a precision gastight syringe.

The reaction was monitored at 245 nm on a Hewlett-Packard 8451 diode array spectrophotometer. The rate constant was determined from a nonlinear least-squares fit of the absorbance–time data to a first-order rate expression. The recorded rate constants are the average of three determinations at each set of conditions. The temperature was controlled by a standard water-jacketed cell holder in the spectrophotometer.

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Registry No. Cu^{2+}, 15158-11-9; Cl^-, 16887-00-6; ascorbic acid, 50-81-7.

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