

115. Cuprous Complexes and Dioxygen

Part 12¹⁾

Rate Law and Mechanism of the Copper-Catalyzed Oxidation of Ascorbic Acid in Aqueous Acetonitrile

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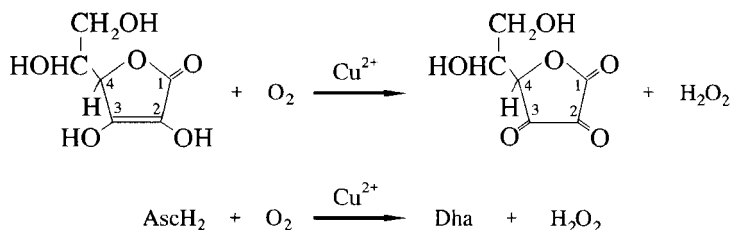
The copper-catalyzed oxidation of ascorbic acid (AscH_2) has been studied with a *Clark* electrode in aqueous MeCN. Cu^{I} or Cu^{II} may be equally used as the source of metal ion, without influence on the rate law. At sufficiently high [MeCN], the rate of the overall reaction is essentially given by the rate of Cu^{I} autoxidation: the reaction is of first order with respect to $[\text{Cu}_{\text{tot}}^{\text{I,II}}]$ and $[\text{O}_2]$ and shows an inverse-square dependence on [MeCN] as observed for the autoxidation of Cu_{aq}^+ . The pH dependence is complicated by the combination of the intrinsic pH effect on autoxidation with an additional term in the rate law which is directly proportional to $[\text{AscH}^-]$. The latter term is explained by direct oxidation of the organic substrate by the primary dioxygen adduct of Cu^{I} , CuO_2^+ . For $[\text{MeCN}] < 0.7\text{M}$, a gradual and pH-dependent transformation of this rate law and deviation from the first-order dependence on $[\text{O}_2]$ is indicated.

Introduction. – Due to its importance in biology and food processing, there has been a great deal of interest in the Cu-catalyzed oxidation of ascorbic acid (AscH_2) by dissolved dioxygen for several decades [2] [3]. Numerous conflicting rate laws and interpretations of experimental data have been published [4–23], and there is no widely accepted mechanism for this obviously complicated reaction. Reported reaction orders are 0.5–1 for $[\text{O}_2]$ and $[\text{Cu}^{\text{II}}]$, 0–1 for $[\text{AscH}_2]$, and –2 to +1 for $[\text{H}^+]$ [3], depending on experimental conditions. Specifically, fractional reaction orders have been used to invoke chain mechanisms with [13] [15] or without [18] reactive radicals as chain carriers. Monovalent Cu has been postulated by the majority of groups involved in this research, but the contrary point of view has also been strongly advocated [2] [13–15].

If Cu^{I} is supposed to be essential in catalytic ascorbate oxidation, the very easy autoxidation of Cu_{aq}^+ [1] [18] [24–26] should be taken into account, and any proposed mechanism should be compatible with the rate law of that latter reaction. With the exception of some preliminary results for media containing high amounts of Cl^- , this does not seem to be the case in general [2] [3]. It is the aim of the present work to firmly establish the role of Cu^{I} autoxidation in the Cu oxidation of ascorbate and to show the full compatibility of the corresponding rate laws in aqueous MeCN. In addition, we hope to have laid a basis for a consistent mechanism of this reaction in the absence of MeCN or other Cu^{I} -stabilizing ligands such as chloride and allyl alcohol, too.

¹⁾ Part 11: [1].

Results. – Contrary to the uncertainties concerning the detailed mechanism, the reaction stoichiometry is firmly established at least for the initial parts of the reaction (*cf.* *Scheme 1*): under the influence of Cu^{2+} ions ascorbic acid is oxidized to dehydroascorbic acid (Dha) and dioxygen reduces to H_2O_2 [2]. Further oxidation of Dha as well as reactions of H_2O_2 are relatively slow processes in weakly acidic solutions and in the presence of excess AscH_2 [9] [21] [22].

Scheme 1

Ascorbic acid (AscH_2) is known to form mono- and di-anionic species, depending on pH. The mono-anion AscH^- forms with deprotonation of the $\text{C}(2)\text{-OH}$ [11].

A total of 161 kinetic measurements were used to vary $[\text{Cu}_{\text{tot}}^{\text{I}}]$, $[\text{Cu}^{\text{II}}]$, $[\text{MeCN}]$, $[\text{AscH}_{2,\text{tot}}]$, and pH within the ranges: $[\text{Cu}_{\text{tot}}^{\text{I}}]$: $8.4 \cdot 10^{-5}$ – $5 \cdot 10^{-4}$ M, $[\text{Cu}^{\text{II}}]$: $2.6 \cdot 10^{-4}$ – $2.1 \cdot 10^{-3}$ M, $[\text{MeCN}]$: 0.68–1.52M, $[\text{AscH}_{2,\text{tot}}]$: $1.0 \cdot 10^{-3}$ – $2.5 \cdot 10^{-2}$ M, pH 2.2–5.1.

Table 1. *Experimental Conditions for Sets of Individual Dependences*

| No. | Parameter varied, range | $[\text{Cu}_{\text{tot}}^{\text{I}}]^{\text{a})}$ $\times 10^{-3}$ [M] | $[\text{MeCN}]$ [M] | $[\text{AscH}_{2,\text{tot}}]$ $\times 10^{-2}$ [M] | pH | Buffer(s) used ^{b)} |
|-----|---|---|------------------------|--|------|---------------------------------|
| 1 | pH 2.2–4.8 | 1.119 | 1.219 | 0.2000 | | CAA, AA |
| 2 | pH 2.4–5.1 | 1.291 | 1.064 | 0.2001 | | CAA, AA |
| 3 | MeCN 0.68–1.52M | 1.028 | | 1.001 | 4.00 | AA |
| 4 | MeCN 0.70–1.51M | 1.034 | | 0.5000 | 2.68 | CAA |
| 5 | Cu^{I} $(0.84\text{--}5.0) \cdot 10^{-4}$ M | | 1.000 | 1.000 | 4.10 | AA |
| 6 | Cu^{I} $(1.1\text{--}5.0) \cdot 10^{-4}$ M | | 1.000 | 1.000 | 2.64 | CAA |
| 7 | Cu^{II} $(0.26\text{--}2.1) \cdot 10^{-3}$ M | | 0.9120 | 1.002 | 4.00 | AA |
| 8 | Cu^{II} $(0.26\text{--}1.8) \cdot 10^{-3}$ M | | 0.8360 | 1.001 | 2.62 | CAA |
| 9 | $\text{AscH}_{2,\text{tot}}$ $(0.10\text{--}2.0) \cdot 10^{-2}$ M | 1.021 | 0.988 | | 4.01 | AA |
| 10 | $\text{AscH}_{2,\text{tot}}$ $(0.12\text{--}2.5) \cdot 10^{-2}$ M | 1.033 | 1.064 | | 2.55 | CAA |
| 11 | CH_3COOH $(0.05\text{--}1.0) \cdot 10^{-1}$ M | 1.022 | 0.988 | 0.5000 | 3.88 | AA |
| 12 | ClCH_2COOH $(0.6\text{--}8) \cdot 10^{-2}$ M | 1.033 | 1.064 | 0.5000 | 2.64 | CAA |

^{a)} Added as Cu^{I} for No. 1; added as Cu^{II} for No. 2–4, and 9–12.
^{b)} AA: CH_3COOH , CAA: ClCH_2COOH . All buffers used are 0.06M.

These experiments were grouped into 10 dependences within which only a single parameter was varied; they are listed in *Table 1*. CH_2ClCOOH and CH_3COOH were used for pH stabilization; experimental conditions for the buffer dependences are also given in *Table 1*. A selection of the 161 experimental points is also shown in *Figs. 2–6*.

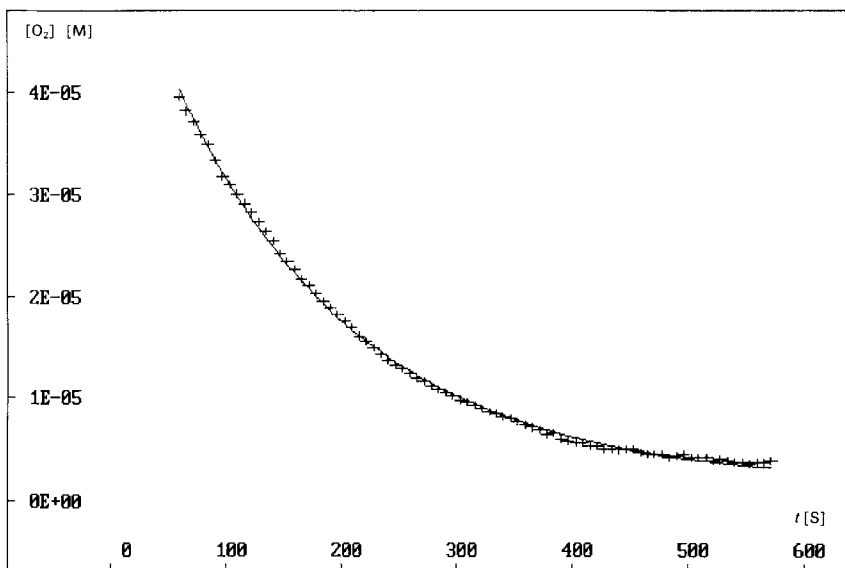


Fig. 1. Consumption of O_2 . +: $[Cu^{II}] = 1.291 \cdot 10^{-3} M$, $[MeCN] = 1.064 M$, $[AscH_{2, tot}] = 2.001 \cdot 10^{-3} M$, pH 2.80; —: calculated with first-order function, $k_{obs} = 6.3 \cdot 10^{-3} s^{-1}$.

Because of the conflicting literature data [3], the reaction order with respect to $[O_2]$ was considered of prime importance in our experiments. As shown in Fig. 1, individual kinetic runs could in general be perfectly described by a simple pseudo-first-order reaction (2). Whenever deviation from Eqn. 2 was observed, e.g. at low pH or low $[MeCN]$ (see below), the corresponding experiments were excluded from the set of data discussed in this work.

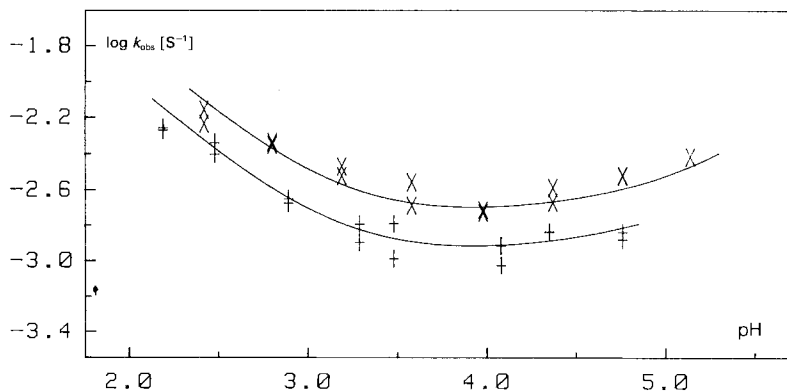


Fig. 2. pH Dependence of $AscH_2$ oxidation. +: $[Cu^{II}] = 1.119 \cdot 10^{-3} M$, $[MeCN] = 1.219 M$, $[AscH_{2, tot}] = 2.000 \cdot 10^{-3} M$; x: $[Cu^{II}] = 1.291 \cdot 10^{-3} M$, $[MeCN] = 1.064 M$, $[AscH_{2, tot}] = 2.001 \cdot 10^{-3} M$; —: calculated with rate law (11), parameter set iii.

The pH dependence of the catalyzed ascorbate oxidation is shown in *Fig. 2*. As discussed recently for the autoxidation of Cu^{I} in the absence of organic substrate [1], we observe a decreasing rate with increasing pH up to 4 and a slight increase again above pH 4.5. While this increase might look questionable upon visual inspection, it is statistically significant at least at the 95% level ($F = 1.36$, $\nu = 155$) for the complete data set. In addition, the value for the corresponding term of the rate law was not extracted from the present set but taken directly from experimental data obtained in the absence of ascorbate [1]. Data below pH 2.2 were excluded, since significant deviation from first-order $[\text{O}_2]$ dependence was noticed in the kinetic runs. As shown in *Fig. 2*, results were similar and could be explained by the same rate law, whether Cu^{I} as $\text{Cu}(\text{MeCN})_4\text{BF}_4$ or Cu^{II} as $\text{Cu}(\text{NO}_3)_2$ were used as the source of copper ions.

Control of pH was effected by ClCH_2COOH and CH_3COOH buffers. As indicated in *Fig. 3*, these had no effect on the rate of reaction at the concentrations employed for the other dependences. This is in line with previous observations that neither Cu^{I} autoxidation [1] [25] nor Cu-catalyzed ascorbate oxidation [6] is influenced by acetate buffers at the concentrations used in this study. In addition, all experimental data could be perfectly described without invoking an additional, buffer dependent term.

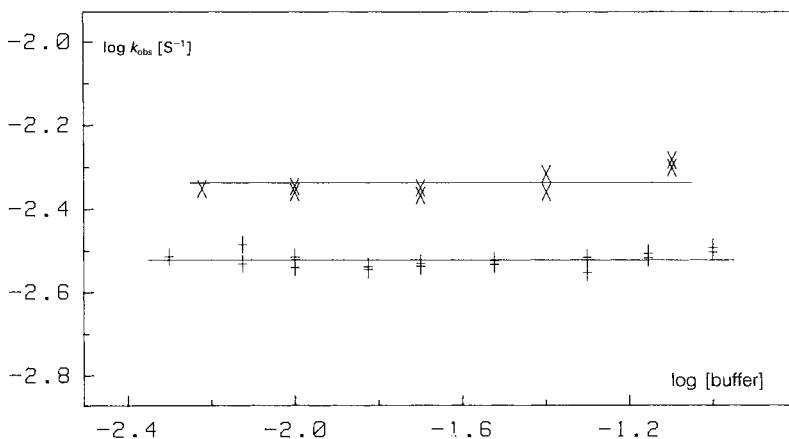


Fig. 3. Influence of buffers on AscH_2 oxidation. +: $[\text{Cu}^{\text{II}}] = 1.022 \cdot 10^{-3} \text{ M}$, $[\text{MeCN}] = 0.988 \text{ M}$, $[\text{AscH}_{2,\text{tot}}] = 5.000 \cdot 10^{-3} \text{ M}$, pH 3.88, CH_3COOH buffer; x: $[\text{Cu}^{\text{II}}] = 1.033 \cdot 10^{-3} \text{ M}$, $[\text{MeCN}] = 1.064 \text{ M}$, $[\text{AscH}_{2,\text{tot}}] = 5.000 \cdot 10^{-3} \text{ M}$, pH 2.64, ClCH_2COOH buffer; —: mean value.

Dependences on $[\text{MeCN}]$ and on $[\text{Cu}^{\text{I}}]$ or $[\text{Cu}^{\text{II}}]$ are given in *Figs. 4* and *5*, respectively. Both at pH 2.68 and at pH 4.00, the rate strongly decreases with increasing $[\text{MeCN}]$, with a slope between -2 and -3 in a double logarithmic presentation. Dependence on copper ion (*Fig. 5*) is of first order both at low and high pH and using Cu^{I} or Cu^{II} as the source of metal ions.

The rate law described so far is qualitatively identical with the recently discussed one for the autoxidation of Cu^{I} in aqueous MeCN, provided that no $\text{Cu}_{\text{aq}}^{2+}$ is present in the solution [1], and one might assume that agreement was not only qualitative but also quantitative. This is, however, not the case: the rate of oxidation is also influenced by the

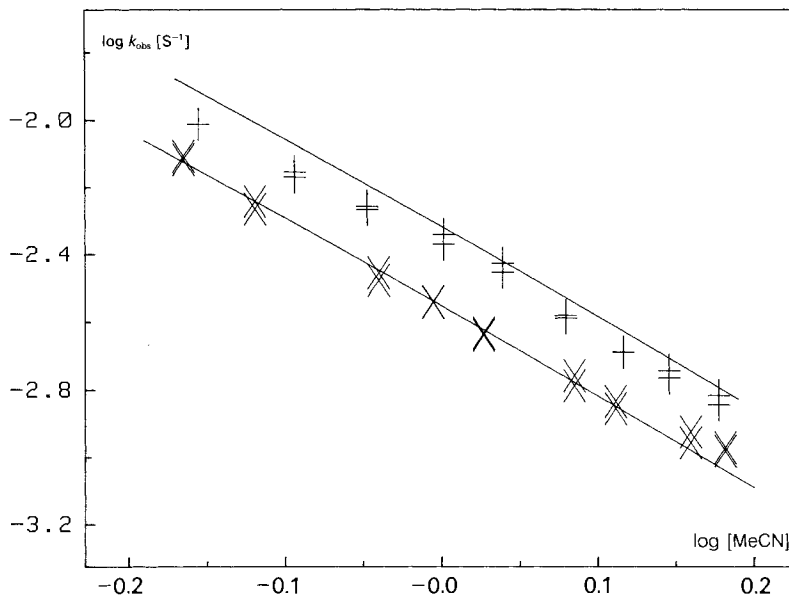


Fig. 4. *MeCN* Dependence of *AscH₂* oxidation. +: $[\text{Cu}^{\text{II}}] = 1.034 \cdot 10^{-3} \text{ M}$, $[\text{AscH}_{2,\text{tot}}] = 5.000 \cdot 10^{-3} \text{ M}$, pH 2.68; x: $[\text{Cu}^{\text{II}}] = 1.028 \cdot 10^{-3} \text{ M}$, $[\text{AscH}_{2,\text{tot}}] = 1.001 \cdot 10^{-2} \text{ M}$, pH 4.00; —: calculated with rate law (11), parameter set *iii*.

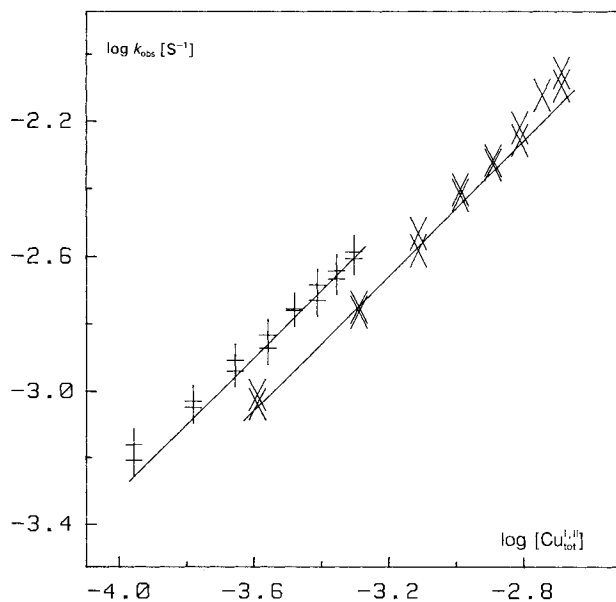


Fig. 5 *Cu^I* and *Cu^{II}* dependences of *AscH₂* oxidation. +: $[\text{MeCN}] = 1.000 \text{ M}$, $[\text{AscH}_{2,\text{tot}}] = 1.000 \cdot 10^{-2} \text{ M}$, pH 2.64, *Cu^I* used; x: $[\text{MeCN}] = 0.912 \text{ M}$, $[\text{AscH}_{2,\text{tot}}] = 1.002 \cdot 10^{-2} \text{ M}$, pH 4.00, *Cu^{II}* used; —: calculated with rate law (11), parameter set *iii*.

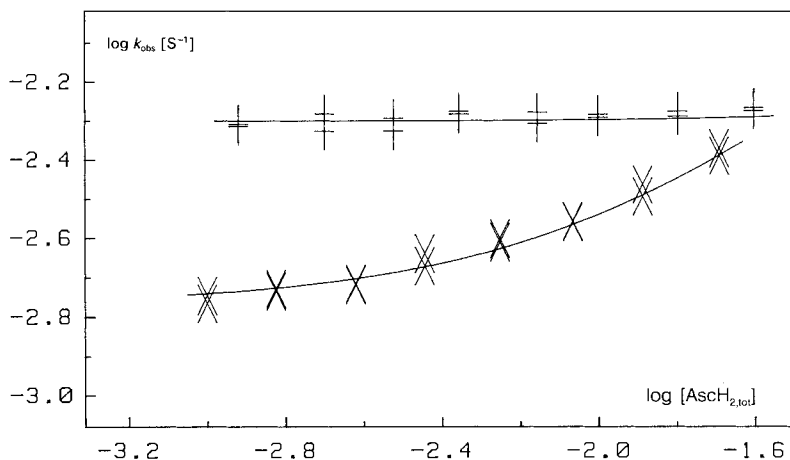
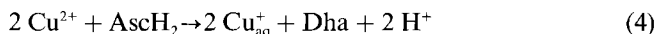
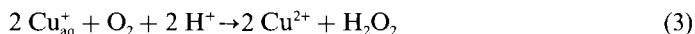


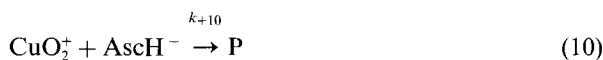
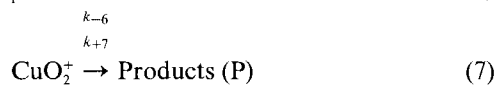
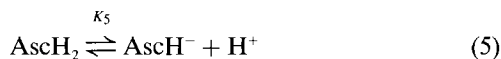
Fig. 6. $AscH_{2,tot}$ Dependence of $AscH_2$ oxidation. +: $[Cu^{II}] = 1.033 \cdot 10^{-3} M$, $[MeCN] = 1.064 M$, pH 2.55; x: $[Cu^{II}] = 1.021 \cdot 10^{-3} M$, $[MeCN] = 0.988 M$, pH 4.01; —: calculated with rate law (11), parameter set iii.

concentration of ascorbate. As shown in Fig. 6, this influence is quite prominent at pH 4 and weak or, rather, nonexistent at pH 2.55.

Based on the data discussed above, the overall reaction stoichiometry, Eqn. 1, can be subdivided into two parts (3) and (4).



The overall rate is given by the slower of the two processes in this 'valence shuttle' reaction [3]. Under the influence of the Cu^I -stabilizing MeCN, Cu_{aq}^+ is complexed to $[Cu(MeCN)_2]^+$ and $[Cu(MeCN)_3]^+$ [25–26], and Cu_{aq}^+ autoxidation (Eqn. 3) becomes rate-determining. The rate of disappearance of O_2 and of formation of products (H_2O_2 , Dha), thus, can be described by the mechanistic steps (5)–(10), i.e. the mechanism describing



Cu_{aq}^+ autoxidation in the absence of $\text{Cu}_{\text{aq}}^{2+}$ [1], supplemented by direct reaction of the dioxygen adduct CuO_2^+ with AscH^- (Eqn. 10). Steady-state elimination of CuO_2^+ gives the theoretical rate law (11). Eqn. 10 and its corresponding term in the rate law (11), thus, are

$$\begin{aligned}
 -d[\text{O}_2]/dt &= k_{+6}[\text{O}_2][\text{Cu}_{\text{aq}}^+] \cdot A/B \\
 &= k_{+6}[\text{O}_2][\text{Cu}_{\text{tot}}^+] \cdot A/B \cdot 1/(\beta_2[\text{MeCN}]^2 + \beta_3[\text{MeCN}]^3) \\
 \text{with} \quad A &= 1 + \frac{k_{+8}}{k_{+7}} [\text{H}^+] + \frac{k_{+9}}{k_{+7}} [\text{OH}^-] + \frac{k_{+10}}{k_{+7}} [\text{AscH}^-], \\
 B &= 1 + \frac{k_{-6}}{k_{+7}} + \frac{k_{+8}}{k_{+7}} [\text{H}^+] + \frac{k_{+9}}{k_{+7}} [\text{OH}^-] + \frac{k_{+10}}{k_{+7}} [\text{AscH}^-], \\
 [\text{AscH}^-] &= K_5 \frac{[\text{AscH}_{2,\text{tot}}]}{K_5 + [\text{H}^+]}
 \end{aligned} \tag{11}$$

the only additions needed to describe the Cu-catalyzed oxidation in the presence of high amounts of MeCN, relative to Cu^+ autoxidation described in [1]. Least-squares estimates of the rate constants are compiled in Table 2, they were obtained from batch calculations of the first 10 dependences listed in Table 1, i.e. from 161 individual kinetic runs. The following calculations were performed: *i*) All parameters besides k_{+10} , i.e. the ascorbate-dependent term were fixed at the values obtained in [1] for Cu^+ autoxidation in the absence of ascorbate. It is rewarding to note that the overall standard deviation $\sigma(\log k_{\text{obs}}) = 0.066$ is even marginally better than the best fit obtained with the original data (0.068) discussed in [1]. *ii*) All parameters were allowed to assume their optimum values with the exception of k_{+6} and of k_{+9}/k_{+7} which again were fixed at the values given in [1], $k_{+6} = 6.5 \cdot 10^6 \text{ M}^{-1} \text{ s}^{-1}$, $k_{+9}/k_{+7} = 5.3 \cdot 10^8 \text{ M}^{-1}$, and k_{+6} and k_{+9}/k_{+7} had to be kept fixed, since experimental restrictions did not allow to determine the corresponding parameters without undue correlation with others. $\sigma(\log k_{\text{obs}}) = 0.047$ is decreased as expected, but at the limit of statistical significance according to the F-test [29]. *iii*) A third calculation was performed with only k_{-6}/k_{+7} and k_{+10}/k_{+7} as adjustable parameters. In this calculation, $\sigma(\log k_{\text{obs}}) = 0.048$ is almost as small as in *ii*, and $k_{-6}/k_{+7} = 7.6 \cdot 10^1$ assumes a value which

Table 2. Parameters of Theoretical Rate Laws

| Parameters | Values reported in [1] | Batch calculations ^{a)} | | | |
|--|--------------------------------|----------------------------------|----------------------------|----------------------------|----------------------------|
| | | <i>i</i> | <i>ii</i> | <i>iii</i> | <i>iv</i> |
| $k_{+6} (\text{M}^{-1} \text{s}^{-1})$ | $(6.5 \pm 0.9) \cdot 10^6$ | [1] | [1] | [1] | [1] |
| $k_{+8}/k_{+7} (\text{M}^{-1})$ | $(1.2 \pm 0.1) \cdot 10^3$ | [1] | $(1.2 \pm 0.1) \cdot 10^3$ | [1] | $(9.4 \pm 0.7) \cdot 10^2$ |
| k_{-6}/k_{+7} | $(8.9 \pm 0.7) \cdot 10^1$ | [1] | $(3.9 \pm 1.1) \cdot 10^1$ | $(7.6 \pm 1.0) \cdot 10^1$ | $(5.9 \pm 1.2) \cdot 10^1$ |
| $\beta_3/\beta_2 [\text{M}^{-1}]^b$ | 1.7 ± 0.3 | [1] | 4.1 ± 1.4 | [1] | 2.3 ± 0.6 |
| $k_{+9}/k_{+7} [\text{M}^{-1}]$ | $(5.3 \pm 1.5) \cdot 10^{8c)}$ | [1] | [1] | [1] | [1] |
| $k_{+10}/k_{+7} [\text{M}^{-1}]^d$ | | $(2.6 \pm 0.1) \cdot 10^2$ | $(1.6 \pm 0.2) \cdot 10^2$ | $(1.8 \pm 0.1) \cdot 10^2$ | $(1.0 \pm 0.2) \cdot 10^2$ |
| $k_{+12}/k_{+10} [\text{M}^{-1}]^d$ | | | | | $(5.6 \pm 1.9) \cdot 10^3$ |
| $\sigma(\log k_{\text{obs}})$ | 0.068 | 0.066 | 0.047 | 0.048 | 0.044 |

^{a)} The parameters fixed are from Cu^+ autoxidation [1].

^{b)} Using $\beta_2(\text{MeCN}) = 10^{4.35}$ [27].

^{c)} Using $K_W = 10^{-13.878}$ [28].

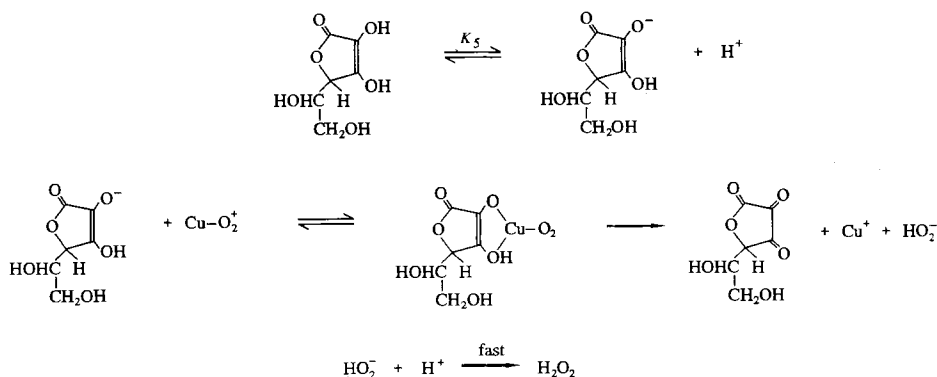
^{d)} Using $K_5(\text{AscH}_2) = 10^{-4.05}$ [11] [14].

is even closer to the one reported previously in the absence of ascorbate ($8.9 \cdot 10^1$ [1]). This set of rate constants was used for the calculation of the theoretical curves in *Figs. 2–5. iv*) An additional calculation was done assuming a proton- and AscH^- -dependent term (12). This again slightly reduced the overall standard deviation, $\sigma(\log k_{\text{obs}}) = 0.044$. The improvement is not statistically significant, however, and in view of the experimental independence of k_{obs} on $[\text{AscH}_{2,101}]$ at low pH (*cf. Fig. 6*), we do not consider k_{+12} to be a likely or even established term. This is in line with previous observations [8] [30] that AscH_2 is about 10^4 times less reactive than AscH^- towards oxidizing agents. Although this statement is valid in the strict sense for outer-sphere mechanisms only, it seems reasonable to exclude AscH_2 as a reactive species from our mechanism.



Discussion. – The results presented here have shown that the Cu-catalyzed oxidation of ascorbate in aqueous MeCN can be described by a valence-shuttle mechanism, (3) and (4), in which Cu^{II} is rapidly reduced by AscH_2 and reoxidation of Cu_{aq}^+ by O_2 described by *Eqns. 6–9* is in the rate-limiting observable step. In addition, a $[\text{AscH}^-]$ -dependent term described by *Eqns. 5 and 10* is firmly established, indicating direct oxidation of ascorbic acid by Cu^{I} and O_2 rather than by Cu^{II} . Neither AscH_2 nor the dianion Asc^{2-} are contributing significantly to the O_2 consumption under our experimental conditions ($[\text{MeCN}] > 0.5\text{M}$, pH 2.5–5). While the present experiments do not reveal any details regarding the $[\text{AscH}^-]$ -dependent step (10), it seems logical to assume electron transfer within a ternary $\text{Cu}_{\text{aq}}^+/\text{O}_2/\text{AscH}^-$ complex. Two-electron transfer, as indicated in *Scheme 2* and leading directly to Dha and H_2O_2 while regenerating Cu^{I} , seems attractive but should not be considered proven at present. We think this cautioning statement to be correct despite several unsuccessful attempts to detect any radicals under analogous conditions [11] [13] [15] [18] [23]. As we have recently shown for the autoxidation of Cu_{aq}^+ [1] in the absence of organic substrate, the corresponding mechanism necessarily includes the formation of one-electron reduction products of O_2 , $\text{O}_2^{\cdot-}$, and HO_2^{\cdot} , which in turn react with Cu^{I} as well as with Cu^{II} in very fast steps close to diffusion control. Under such conditions, trapping agents or superoxide dismutase may easily fail to show a significant effect, especially as the above-mentioned radicals would act as simple intermediates and not as essential chain carriers.

Scheme 2



Copper-catalyzed ascorbate oxidation *can* be first order with respect to $[O_2]$, and Cu^I autoxidation *can* be the rate-limiting step of the overall reaction in the presence of enough MeCN or Cl^- [3]. Nevertheless, this *cannot* be the complete story of the reaction. Half-order dependence on $[O_2]$ is established beyond doubt [15] [16] [18], and deviation of experimental curves in that direction has been observed in the present work, notably at low pH (< 2.5) and at low [MeCN] ($< 0.7M$). These are experimental conditions which favor fast autoxidation of Cu^I and at the same time are thermodynamically unfavorable for ascorbate oxidation by Cu^{II} . This is shifting the overall equilibrium from the Cu^I to the Cu^{II} state, *i.e.* the stoichiometric Eqn. 4 might become rate-limiting instead of Eqn. 3.

When Cu^{II} is present in excess over Cu^I , the full and complicated rate law of autoxidation discussed in [1] gets operative with concomitant O_2 reduction in one-electron steps *via* $\cdot O_2^-$ or HO_2 and in a two-electron step *via* binuclear $Cu_2O_2^{2+}$. In view of the half-order dependence on O_2 found by several researchers, a chain mechanism made up of the species and reaction steps described in the present work and in [1] is likely to be operative. A proposal in this direction has indeed been made by *Shtamm et al.* [18] several years ago, based on the erroneous assumption of irreversible formation of the primary dioxygen adduct, CuO_2^+ , and neglecting the pH-dependent terms of Cu^I autoxidation. Simply making formation of CuO_2^+ reversible as indicated in Eqn. 6 instead of irreversible would not be compatible with the rate law (13) published by these authors as well as by *Jameson*

$$-d[O_2]dt = k_{+13}[Cu^{2+}][AscH^-][O_2]^{1/2} \quad (13)$$

and *Blackburn* [15] [16] who have advocated a rather different chain mechanism without the intermediacy of Cu^I . To finally settle the question of the Cu-catalyzed ascorbate oxidation in the absence of Cu^I stabilizing ligands, too, additional experiments and careful reconsideration of published data will be necessary on the basis of the results described in this work and also for Cu^I autoxidation in the presence of a large excess of Cu^{II} [1]. It seems easy to predict that the corresponding rate law will be multitermed and complicated, but we are confident that interaction of O_2 with Cu_{aq}^+ again will play a central role in the mechanism.

Experimental. – $Cu(MeCN)_4BF_4$ was synthesized according to [1] [31] and stored as a sat. soln. in pure MeCN. $Cu(NO_3)_2$: *p.A.* The stock soln. was kept in a weakly acidic HNO_3 soln. Concentrations of Cu^I and Cu^{II} were determined by spectrophotometric titration with EDTA in acetate buffer. *L*-Ascorbic acid ($AscH_2$): *p.A.* The stock soln., *ca.* $5 \cdot 10^{-2} M$, was freshly prepared every day. MeCN: *p.A.* was kept dry by 3-Å molecular sieves. KNO_3 : *p.A.* pH was adjusted to the desired values using buffers based on $ClCH_2COOH$ and CH_3COOH in combination with NaOH. The temp. and ionic strength of the reaction system were $25 \pm 0.1^\circ$ and $I = 0.5$, resp.

Instrumentation and Calculations. Kinetic traces of O_2 consumption were obtained using a Clark electrode and instrumentation described in [1]. Complete reaction curves were obtained at the high and the low end of the parameter varied in each set (*cf. Table 1*) in order to check for first-order dependence on $[O_2]$. When the corresponding limits were established, the other experiments could be stopped earlier. Then, they were evaluated by the least-squares method given in [1] where a description of the fitting procedure and of the definition of the overall variance $\sigma^2(\log k_{obs})$ may also be found.

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