160. Cuprous Complexes and Dioxygen

Part 11[1])

Concomitant One- and Two-Electron Reduction of O_2 by the Cu_{aq}^+ Ion

by **Li Mi** and **Andreas D. Zuberbühler***

Institut für Anorganische Chemie der Universität, Spitalstrasse 51, CH-4056 Basel

(12.IX.91)

The autoxidation of Cu^I in aqueous MeCN has been studied using a *Clark* oxygen electrode in the presence and absence of Cu^{II}. The reaction is inhibited by Cu^{II} in the pH range of 0.5 to 5.0, reaching a lower limiting value at the highest concentrations. The reaction order changes from 1 to 2 with respect to Cu^I under the influence of Cu^{2+} ion. Detailed kinetics analysis of a total of 275 measurements has shown that an unstable primary adduct CuO_2^+ decomposes to give $^{\cdot}O_2^-$ or $HO_2^{\cdot}$, depending on pH, and also reacts directly with a second Cu^+ ion, avoiding one-electron reduction of O_2 by this path. Reaction of $HO_2^{\cdot}$ is faster with Cu^I than with Cu^{II} by a factor of 20, and single-electron transfer within CuO_2^+ to Cu^{2+} and $^{\cdot}O_2^-$ predominates over reaction with a second copper ion for $[Cu^I_{tot}] < 2 \cdot 10^{-3}$ M in the absence of Cu^{2+}. The most likely value for the reaction of $^{\cdot}O_2^-$ with Cu^I is $5.3 \cdot 10^8$ $M^{-1}s^{-1}$, but even this high rate constant is at the limit of significance. All secondary reactions following the initial formation of CuO_2^+ are shown to be very fast, a fact that should be properly considered in the discussion of mechanisms of copper-catalyzed oxidations and oxygenations.

Introduction. – The interaction of dioxygen with Cu^I complexes and the autoxidation of Cu^I both play a central role in the copper-catalyzed oxidation of organic substrates [2–12]. Recently, remarkable progress has been made in the study of quasireversible copper-dioxygen interaction in organic solvents [4] [13]. Nevertheless, these species in general only have a fleeting existence, at least at room temperature and in H_2O [2]. In addition, the one-electron reduction products of O_2, $^{\cdot}O_2^-$, and $HO_2^{\cdot}$, are very reactive towards copper ions and simple copper complexes [14–19], which thus may behave as efficient superoxide dismutases [20]. Not surprising, detailed mechanisms of copper-catalyzed oxidations based on dioxygen are often disputed. Experiments excluding $^{\cdot}O_2^-$ and $HO_2^{\cdot}$ from such reactions based on negative results with radical trapping agents [12] may be inconclusive, because of the high reactivity of copper complexes towards these species. This ambiguity pertains even to simple solvated copper ions, despite the considerable effort put into the autoxidation of Cu_{aq}^+ [21–23]. Radical-free chain mechanisms based on CuO_2^+ as the reactive species have been postulated for the catalytic oxidation of both ascorbic acid [9] and catechol [12], but the corresponding chain termination by a second copper ion has so far not been backed by the *experimental rate law* (*1*), as discussed in [2].

---

[1] Part 10: [1].

$$-d[O_2]/dt = \frac{k_a[Cu^I_{tot}][O_2](1+k_b[H^+])}{(1+k_c[H^+])(\beta_2[MeCN]^2+\beta_3[MeCN]^3)} \tag{1a}$$

$$= \frac{k_a[Cu^+_{aq}][O_2](1+k_b[H^+])}{1+k_c[H^+]} \tag{1b}$$

$$\log\beta_2 = 4.35\ [24],\ \log\beta_3 = 4.39\ [22]$$

Second-order dependence on reduced copper consistent with a dimeric species $[Cu(L)]_2O_2$ has been repeatably observed [5] [25–27], however, and effective competition between one- and two-electron reduction has been established for a series of substituted imidazoles [18] [19]. It is the aim of this work to show that the same type of competitions is operating in the autoxidation of solvated Cu^I, Cu^+_{aq}, laying an unequivocal basis for future studies on the catalytic activity of this ion.

Results. – Depending on the experimental conditions, dioxygen may be reduced primarily to H_2O_2 (*2*) or to H_2O (*3*) by Cu^I.

$$2Cu^I + 2H^+ + O_2 \rightarrow 2Cu^{II} + H_2O_2 \tag{2}$$

$$4Cu^I + 4H^+ + O_2 \rightarrow 4Cu^{II} + 2H_2O \tag{3}$$

As all reaction curves were treated to obtain pseudo-first-order rate constants k_{obs} (*4*)

$$k_{obs} = \frac{-d[O_2]}{dt \cdot [O_2]} \tag{4}$$

based on initial rates calculated by nonlinear least-squares analysis of the early parts of the reactions (*cf. Experimental*), the actual reaction stoichiometry had no effect on the results and was in general not determined. In fact, most experiments were performed with substoichiometric amounts of dioxygen, precluding any attempts to determine this ratio.

A total of 275 kinetic runs were used to vary $[Cu^I_{tot}]$ ($8.8 \cdot 10^{-5}$–$5.4 \cdot 10^{-4}$ M), $[Cu^{2+}]$ (10^{-4}–$5 \cdot 10^{-2}$ M), [MeCN] (0.14–1.1 M), and pH (0.28–5.1), and to deduce the experimental rate law. The addition of MeCN was necessary to avoid disproportionation of Cu^I and to bring the rate of autoxidation into a convenient range, as only Cu^+_{aq}, but not the various MeCN complexes are directly reactive towards O_2 [22]. 121 experiments were done in the absence, 154 in the presence of Cu^{II}. They were grouped into 16 different sets within which only a single parameter was varied. It was independently checked that the buffer acids $CHCl_2COOH$, $CH_2ClCOOH$, and CH_3COOH used for pH stabilization had no significant influence on the rate law. The experimental conditions for the 16 sets of experiments are collected in *Table 1*.

Three main sets of calculations were performed on the data: *i*) the experiments without addition of Cu^{2+} were used to check the published rate law (*1*) and to optimize the parameters for the conditions (temperature, ionic strength) of this work. *ii*) Additional parameters were calculated including the data of solutions with Cu^{2+} and using several rate laws derived from different mechanistic schemes. *iii*) For some of the rate laws the complete set of kinetic parameters was simultaneously optimized based on the total set of data. The main results are collected in *Table 2*.

As can be seen from *Table 2*, the results obtained in the absence of Cu^{2+} are essentially as described by the rate law (*1*) [22]. Differences in the parameters are relatively small and

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

No.	Parameter varied, range	$[Cu^I_{tot}]$ [$\cdot 10^{-4}$ M]	[MeCN] [M]	$[Cu^{2+}]$ [$\cdot 10^{-2}$ M]	pH	Buffer(s)[a]) used
1	pH 0.3–1.7	2.973	1.207	0		NA, var.
2	pH 1.5–3.1	2.973	0.7055	0		DAA, CAA, 0.06M
3	pH 2.2–5.0	2.933	0.3000	0		CAA, AA, 0.06M
4	MeCN 0.3–1.1M	2.973		0	2.71	CAA, 0.06M
5	Cu^I (0.89–5.4) $\cdot 10^{-4}$ M		0.8000	0	2.76	CAA, 0.06M
6	MeCN 0.2–1.0M	2.973		0	3.93	AA, 0.06M
7	Cu^I (0.89–5.4) $\cdot 10^{-4}$ M		0.8000	0	3.95	AA, 0.06M
8	pH 0.3–1.7	2.973	1.207	2.000		NA, var.
9	pH 1.5–2.9	2.973	0.7055	2.000		DAA, CAA 0.1M
10	pH 2.4–5.1	2.924	0.2935	2.000		CAA, AA, 0.1M
11	Cu^I (0.88–5.4) $\cdot 10^{-4}$ M		0.3000	2.000	2.47	CAA, 0.1M
12	Cu^I (0.88–5.3) $\cdot 10^{-4}$ M		0.3000	2.000	4.33	AA, 0.1M
13	Cu^{II} (0.05–5.0) $\cdot 10^{-2}$ M	2.973	0.3000		2.65	CAA, 0.1M
14	Cu^{II} (0.01–5.0) $\cdot 10^{-2}$ M	2.924	0.3011		3.85	AA, 0.1M
15	MeCN 0.14–0.9M	4.197		2.000	3.55	AA, 0.1M
16	MeCN 0.22–0.92M	3.546		2.027	2.56	CAA, 0.1M

[a]) AA: AcOH, CAA: $CH_2ClCOOH$, DAA: $CHCl_2COOH$, NA: HNO_3.

Table 2. *Parameters of Theoretical Rate Laws*

Rate constants	Results without Cu^{II}			Mechanism *a*[a])		Mechanism *b*, *c*[a])	
	without 1/[H$^+$] term	with 1/[H$^+$] term	[22][f])	without 1/[H$^+$] term	with 1/[H$^+$] term	without 1/[H$^+$] term	with 1/[H$^+$] term
k_{+5}	$(7.8 \pm 1.1) \cdot 10^6$	$(6.5 \pm 0.9) \cdot 10^6$	$9.5 \cdot 10^5$	$(5.8 \pm 0.6) \cdot 10^6$	$(5.3 \pm 0.5) \cdot 10^6$	$(5.7 \pm 0.6) \cdot 10^6$	$(5.0 \pm 0.5) \cdot 10^6$
k_{+11}/k_{+7}	–	–	–	$(3.9 \pm 0.3) \cdot 10^2$	$(3.4 \pm 0.3) \cdot 10^2$	$(5.1 \pm 0.3) \cdot 10^2$	$(4.3 \pm 0.4) \cdot 10^2$
k_{-6}/k_{+9}	–	–	–	$(4.3 \pm 0.2) \cdot 10^{-2}$	$(4.3 \pm 0.2) \cdot 10^{-2}$	$(4.3 \pm 0.3) \cdot 10^{-2}$	$(4.6 \pm 0.2) \cdot 10^{-2}$
k_{+10}/k_{-7}	–	–	–	2.0 ± 0.4	2.1 ± 0.4	< 5	< 5
k_{-7}/k_{+9}	–	–	–	–	–	2.8 ± 0.4[b])	1.8 ± 0.3[b])
k_{+6}/k_{+7}[c])	$(1.0 \pm 0.1) \cdot 10^3$	$(1.2 \pm 0.1) \cdot 10^3$	$4.1 \cdot 10^2$	$(1.2 \pm 0.1) \cdot 10^3$	$(1.3 \pm 0.1) \cdot 10^3$	$(1.2 \pm 0.1) \cdot 10^3$	$(1.4 \pm 0.1) \cdot 10^3$
k_{-5}/k_{+7}[c])	$(8.8 \pm 0.8) \cdot 10^1$	$(8.9 \pm 0.7) \cdot 10^1$	$2.7 \cdot 10^1$	$(8.1 \pm 0.6) \cdot 10^1$	$(8.2 \pm 0.5) \cdot 10^1$	$(8.4 \pm 0.6) \cdot 10^1$	$(8.7 \pm 0.6) \cdot 10^1$
k_{-6}/k_{-7}[d])	–	–	–	–	–	$1.5 \cdot 10^{-2}$[b])	$2.6 \cdot 10^{-2}$[b])
β_3/β_2[c])	2.1 ± 0.3	1.7 ± 0.3	1.1	1.8 ± 0.2	1.7 ± 0.2	1.7 ± 0.2	1.5 ± 0.1
σ (log k_{obs})	0.073	0.068	–	0.072	0.066	0.074	0.067

[a]) The 'best' reactivity ratios of $Cu(MeCN)_2^+$ and $Cu(MeCN)_3^+$ were 1.1:1 in mechanism *a* and 1.5:1 in mechanism *b*, and *c*, respectively.

[b]) Relates to mechanism *c*, using log $K_{12} = 4.8$ [29–31]. With mechanism *b*, these entries have to be replaced by $k_{-7}/k_9 \cdot K_{12}$ and $k_{-6}/k_{-7}/K_{12}$, respectively.

[c]) For the rate constants without Cu^{II}: k_{6a}/k_{7a} and k_{-5}/k_{7a} instead of k_{+6}/k_{+7} and k_{-5}/k_{+7}, respectively.

[d]) $k_{-6}/k_{-7} = (k_{-6}/k_{+9})/(k_{-7}/k_{+9})$.

[e]) $\beta_2 = 10^{4.35}$ [22] [24].

[f]) Without 1/[H$^+$] term.

may be easily attributed to changes in temperature (298 K, [22]: 293 K), ionic strength (0.5M, [22]: 0.2M), and inert electrolyte (KNO_3, [22]: Na_2SO_4). Rate law *(1)* can be rationalized by the series of mechanistic steps *(5)*, *(6a)*, and *(7a)* in which details of the

$$\mathrm{Cu^+_{aq} + O_2 \underset{k_{-5}}{\overset{k_{+5}}{\rightleftharpoons}} CuO_2^+} \tag{5}$$

$$\mathrm{CuO_2^+ + H^+ \xrightarrow{k_{6a}} P} \tag{6a}$$

$$\mathrm{CuO_2^+ \xrightarrow{k_{7a}} P} \tag{7a}$$

conversion to the products Cu^{2+}_{aq} and H_2O_2 are not specified. As shown in *Table 2*, the published rate law has been supplemented by an additional base dependent term *(8a)* to

$$\mathrm{CuO_2^+ + OH^- \xrightarrow{k_{8a}} P} \tag{8a}$$

improve the fit of data with the highest accessible pH values (4.5–5.0). This term is at the limit of significance and not central to the following mechanistic considerations. The situation changes fundamentally, when the autoxidation is performed in the presence of large amounts of Cu^{2+}_{aq}. As shown in *Fig. 1*, small (roughly stoichiometric) amounts of this ion do not interfere, but significant inhibition is observed with a ten- to hundred-fold excess of Cu^{2+}_{aq}. The inhibition begins later at low than at high pH; in the latter case a lower limiting value is indicated for $[Cu^{2+}_{aq}] > 10^{-2}$M. Under the influence of Cu^{2+}_{aq}, the reaction order with respect to $[Cu^I]$ changes from +1 to +2, as shown in *Fig. 2*.

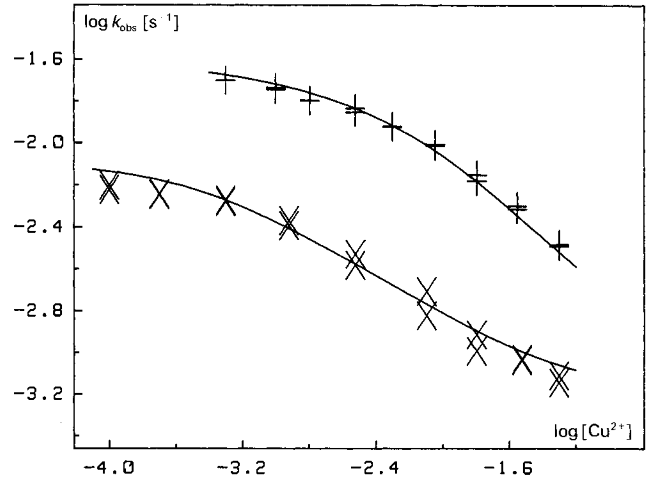

Fig. 1. *Cu^{2+} Dependence of Cu^I autoxidation.* +: $[Cu^I_{tot}] = 3.0 \cdot 10^{-4}$ M, [MeCN] = 0.3M, pH = 2.65; ×: $[Cu^I_{tot}] = 2.9 \cdot 10^{-4}$ M, [MeCN] = 0.3M, pH = 3.85. ——: calculated with rate law *(13)*.

At the same time, the $1/[H^+]$ term in the high pH region seems to become more prominent and, surprisingly, the dependence on [MeCN] does not change, *cf. Figs. 3* and *4*.

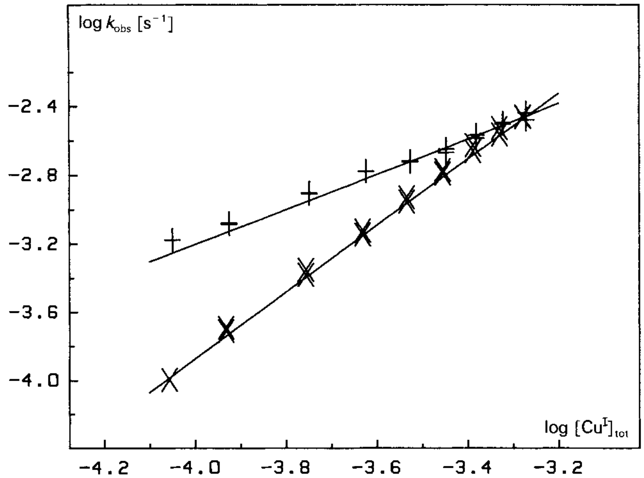

Fig. 2. *Cu^+ Dependence of Cu^I autoxidation.* +: [MeCN] = 0.8M, pH = 2.76, no Cu^{2+} added; ×: [MeCN] = 0.3M, pH = 4.33, [Cu^{2+}] = 0.02M. ——: calculated with rate law (*13*).

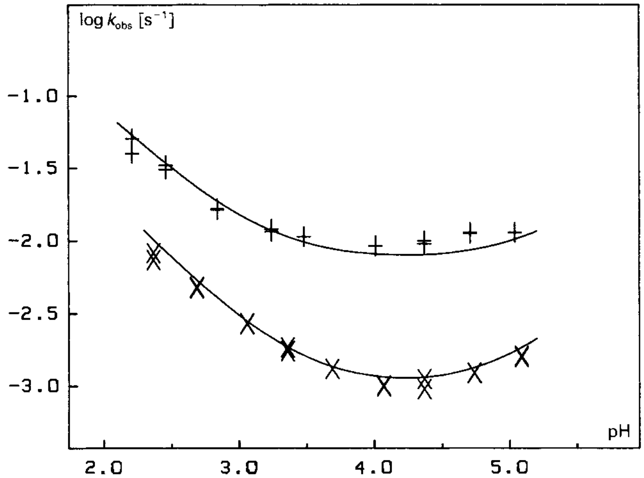

Fig. 3. *pH Dependence of Cu^I autoxidation.* +: [Cu^I_{tot}] = 2.9 · 10^{-4} M, [MeCN] = 0.3M, no Cu^{2+} added; ×: [Cu^I_{tot}] = 2.9 · 10^{-4} M, [MeCN] = 0.29M, [Cu^{2+}] = 0.02M. ——: calculated with rate law (*13*).

Together with the second-order dependence on [Cu^I], the unchanged [MeCN] dependence means that any follow-up interactions with a second Cu^I ion do not involve Cu^+_{aq}, but the predominating species $Cu(MeCN)^+_2$ and $Cu(MeCN)^+_3$ which in combination essentially represent the analytical concentration of Cu^I: $[Cu^I_{tot}] \approx [Cu(MeCN)^+_2] + [Cu(MeCN)^+_3]$ under our experimental conditions. While predominant reactivity of Cu^+_{aq} and $Cu(MeCN)^+$ can be excluded by these findings, we have also tried to calculate individual rate constants for $Cu(MeCN)^+_2$ and $Cu(MeCN)^+_3$, with negative outcome: the 'best' reactivity ratio was 1.1–1.5:1 with an estimated standard error easily including

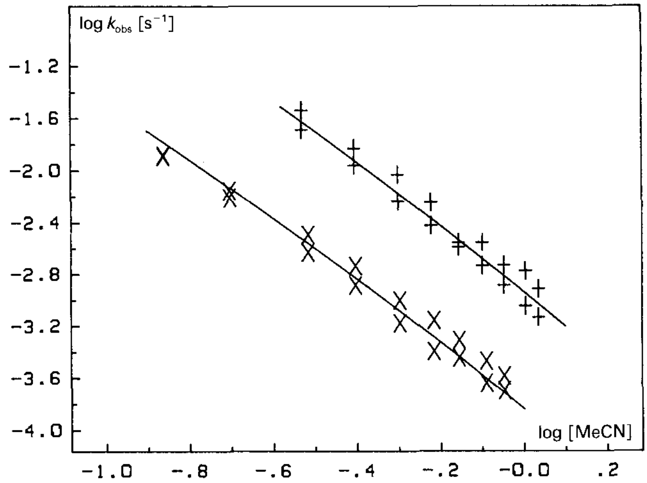

Fig. 4. *MeCN Dependence of Cu^I autoxidation.* +: $[\mathrm{Cu}^{\mathrm{I}}_{\mathrm{tot}}] = 2.9 \cdot 10^{-4}$ M, pH = 2.71, no Cu^{2+} added; ×: $[\mathrm{Cu}^{\mathrm{I}}_{\mathrm{tot}}] = 4.2 \cdot 10^{-4}$ M, pH = 3.55, $[\mathrm{Cu}^{2+}] = 0.02$M. ——: calculated with rate law (*13*).

unity and practically no improvement in overall fit. Retaining *Eqn. 5*, the preliminary mechanistic steps (*6a*)–(*8a*) can be replaced by a chemically detailed mechanistic scheme (*6*)–(*12*) with $[\mathrm{Cu}^{\mathrm{I}}_{\mathrm{tot}}]$ as indicated above based on this evidence. The mechanistic scheme (*5*)–(*12*) was tested using the complete set of 275 data points after steady-state elimination of the intermediates CuO_2^+, $\mathrm{HO}_2^{\cdot}$, and $^{\cdot}\mathrm{O}_2^-$.

$$\mathrm{CuO}_2^+ + \mathrm{H}^+ \xrightleftharpoons[k_{-6}]{k_{+6}} \mathrm{Cu}^{2+}_{\mathrm{aq}} + \mathrm{HO}_2^{\cdot} \qquad (6)$$

$$\mathrm{CuO}_2^+ \xrightleftharpoons[k_{-7}]{k_{+7}} \mathrm{Cu}^{2+}_{\mathrm{aq}} + {}^{\cdot}\mathrm{O}_2^- \qquad (7)$$

$$\mathrm{CuO}_2^+ + \mathrm{OH}^- \xrightarrow{k_{+8}} \mathrm{Cu}^{2+} + {}^{\cdot}\mathrm{O}_2^- \ (+\mathrm{OH}^-) \qquad (8)$$

$$\mathrm{Cu}^{\mathrm{I}}_{\mathrm{tot}} + \mathrm{HO}_2^{\cdot} \xrightarrow{k_{+9},\,\mathrm{H}^+} \mathrm{Cu}^{2+} + \mathrm{H}_2\mathrm{O}_2 \qquad (9)$$

$$\mathrm{Cu}^{\mathrm{I}}_{\mathrm{tot}} + {}^{\cdot}\mathrm{O}_2^- \xrightarrow{k_{+10},\,2\,\mathrm{H}^+} \mathrm{Cu}^{2+} + \mathrm{H}_2\mathrm{O}_2 \qquad (10)$$

$$\mathrm{Cu}^{\mathrm{I}}_{\mathrm{tot}} + \mathrm{CuO}_2^+ \xrightarrow{k_{+11},\,2\,\mathrm{H}^+} \mathrm{Cu}^{2+} + \mathrm{H}_2\mathrm{O}_2 \qquad (11)$$

$${}^{\cdot}\mathrm{O}_2^- + \mathrm{H}^+ \xrightleftharpoons{K_{12}} \mathrm{HO}_2^{\cdot} \qquad (12)$$

Several reduced schemes were tried, specifically leaving out k_{-6}, k_{-7}, k_{+9}, k_{+10}, k_{+11}, or K_{12}. Omission of any of the above parameters was unacceptable, based on visual inspection as well as on the overall variance (*F* test, [28]) with the exception of the superoxide protonation constant K_{12}. Protonation of $^{\cdot}\mathrm{O}_2^-$ was in effect included in several ways into the rate law: *a*) using CuO_2^+, $\mathrm{HO}_2^{\cdot}$, and $^{\cdot}\mathrm{O}_2^-$ as three independent steady-state species, *i.e.* neglecting equilibration between $\mathrm{HO}_2^{\cdot}$ and $^{\cdot}\mathrm{O}_2^-$ according to (*12*), *b*) assuming $\mathrm{HO}_2^{\cdot}$ and CuO_2^+ to be the only steady-state species, but replacing $[^{\cdot}\mathrm{O}_2^-]$ by $[\mathrm{HO}_2^{\cdot}]/[\mathrm{H}^+]$, *c*) using the published value of $\log K_{12} = \log K^{H} = 4.8$ [29–31] or 4.5 [32]. All three possibilities lead to rather similar rate laws, and the results could not be distinguished by the quality of fit between experimental data and calculated values. Possibility *a* implicitely means that reaction of $^{\cdot}O_2^-$ with H^+ is not much faster than with Cu^+ and Cu^{2+}. This would not be completely absurd, since the latter are very fast reactions, and concentrations of copper ions are considerably higher than $[H^+]$ at least at the higher pH values where the contribution of $^{\cdot}O_2^-$ becomes relevant. The possibilities *a–c* all were in addition tested with and without the $1/[H^+]$ term arising from the deprotonation of CuO_2^+ (*8*), with a similar result in all cases: the fit, especially in the high range of pH improves, but at the limit of significance ($\sigma(\log k_{obs}) = 0.067$ *vs.* 0.074 for meachnisms *b* and *c*). The theoretical rate law based on the mechanistic steps (*5*)–(*11*), *i.e.* without equilibration of $HO_2^{\cdot}$ and $^{\cdot}O_2^-$ is given by (*13*).

$$\begin{aligned} -d[O_2]/dt &= k_{+5}[O_2][Cu^+_{aq}][Cu^I_{tot}] \cdot A/B \\ &= k_{+5}[O_2][Cu^I_{tot}]^2 \cdot A/B \cdot 1/(\beta_2[MeCN]^2 + \beta_3[MeCN]^3) \end{aligned} \tag{13}$$

$$\begin{aligned} \text{with } A &= k_{+11}/k_{+7} \cdot (k_{-6}/k_{+9} \cdot [Cu^{2+}] + [Cu^I_{tot}])(k_{-7}/k_{+10} \cdot [Cu^{2+}] + [Cu^I_{tot}]) + \\ &\quad k_{+6}/k_{+7} \cdot [H^+] \cdot (k_{-7}/k_{+10} \cdot [Cu^{2+}] + [Cu^I_{tot}]) + (k_{-6}/k_{+9} \cdot [Cu^{2+}] + [Cu^I_{tot}]) \\ \text{and } B &= (k_{+11}/k_{+7} \cdot [Cu^I_{tot}] + k_{-5}/k_{+7}) \cdot (k_{-6}/k_{+9} \cdot [Cu^{2+}] + [Cu^I_{tot}]) \cdot \\ &\quad (k_{-7}/k_{+10} \cdot [Cu^{2+}] + [Cu^I_{tot}]) + k_{+6}/k_{+7} \cdot [H^+] \cdot [Cu^I_{tot}] \cdot \\ &\quad (k_{-7}/k_{+10} \cdot [Cu^{2+}] + [Cu^I_{tot}]) + [Cu^I_{tot}] \cdot (k_{-6}/k_{+9} \cdot [Cu^{2+}] + [Cu^I_{tot}]) \end{aligned}$$

Discussion. – Very high reactivity of one-electron reduction products of O_2 with both Cu^+_{aq} and Cu^{2+}_{aq} has long been known from independent studies [9] [15–17], and copper ions have been classified as efficient superoxide dismutases [3]. The present work fully substantiates these findings as an integral part of the mechanistic scheme of Cu^I autoxidation. As long as Cu^I predominates over Cu^{II}, the paths governed by consecutive one-electron reduction of O_2 are predominant, and mechanistic schemes of copper-catalyzed oxidations, *e.g.* of ascorbate, should be considered with reservation and assumed incomplete without such steps. When Cu^{II} is in large excess over Cu^I, the situation is different. Now, the one-electron path is blocked by the back reactions (*cf.* (*6*) and (*7*)), and a path including a binuclear transition state (*11*) predominates. No chemical evidence for a species $Cu_2O_2^{2+}$ has been obtained, but it is reasonable to assume that (*11*) preceeds *via* innersphere electron transfer, especially in view of the rapid progress made in the characterization of binuclear μ-peroxo complexes in organic solvents and mainly at reduced temperature [4] [5] [13].

Literature values being reported for reactions of Cu^{2+}_{aq} with $HO_2^{\cdot}$ (k_{-6}: $1.5 \cdot 10^7 \text{M}^{-1}\text{s}^{-1}$ [15], $1.2 \cdot 10^8 \text{M}^{-1}\text{s}^{-1}$ [16], $3.4 \cdot 10^7 \text{M}^{-1}\text{s}^{-1}$ [14] [17]) and with $^{\cdot}O_2^-$ (k_{-7}: $2.5 \cdot 10^8 \text{M}^{-1}\text{s}^{-1}$ [15]), as well as of Cu^+_{aq} with $HO_2^{\cdot}$ (k_{+9}: $6 \cdot 10^8 \text{M}^{-1}\text{s}^{-1}$ [15], $2.3 \cdot 10^9 \text{M}^{-1}$ s^{-1} [17]), it is attractive to compare these data with our own results. As indicated in *Table 2*, the outcome is quite acceptable: the ratios of k_{-6}/k_{-7} are 0.015–0.026, depending on the rate law used and 0.06 [15]; for k_{-6}/k_{+9} we obtain 0.043–0.046 against 0.025 [15]. It would be unfair to expect any better agreement, considering the differences in laboratories, analytical methods, and experimental conditions, as well as taking into account the uncertainties of the reported values as indicated above.

The mechanistic scheme *a* ((*5*)–(*11*)) also yields a value for the relative reactivity of $^{\cdot}O_2^-$ with Cu^I and Cu^{II}: $k_{+10}/k_{-7} = 2.1$. From this and the literature data for k_{-7} [15], we could deduce $k_{+10} = 5.3 \cdot 10^8 \mathrm{M}^{-1}\mathrm{s}^{-1}$. Based on charge effects, it would be quite reasonable to postulate that the ratio of Cu^I *vs.* Cu^{II} reactivity would be higher with the neutral species $HO_2^{\cdot}$ than towards $^{\cdot}O_2^-$. However, this part is inconclusive at present. Determination of k_{+10}/k_{-7} depends specifically on the selection of model *a*, *i.e.* without equilibration of $HO_2^{\cdot}$ and $^{\cdot}O_2^-$. As soon as the latter is allowed for, there arise additional terms in the rate law in competition with k_{+10}/k_{-7}. While the above value remains in the range of possibilities, we must accept that even completely neglecting k_{+10} makes no significant difference. This is not true in the opposite direction, $k_{+10}/k_{-7} > 5$ can be safely excluded based on all mechanistic schemes.

Other entries of *Table 2* may be commented upon as follows. *a*) Goodness of fit is practically identical for the complete set of data and for the subset containing no Cu^{2+}. We, thus, have every reason to assume that no significant term or elementary step is missing in our rate law. *b*) The rate of formation of CuO_2^+ (k_{+5}) is increased relative to the reported values [22]. This may in part be due to a change in the formation constant β_2 ($10^{4.35}$ [24]) which was not redetermined in this work. *c*) One-electron decomposition of CuO_2^+ (k_{+7}) competes with reaction with a second Cu^I (k_{+11}): $k_{+11}/k_{+7} = 340–510 \mathrm{M}^{-1}$. We, thus, would expect second-order dependence for $[Cu^I_{tot}] > 2 \cdot 10^{-3} \mathrm{M}$ even in the absence of Cu^{2+}, but such conditions are not experimentally accessible with our setup. *d*) Other terms pertain to the relative reactivity of CuO_2^+ to form $HO_2^{\cdot}$ and $^{\cdot}O_2^-$ ($k_{+6}/k_{+7} = 1.0–1.4 \cdot 10^3 \mathrm{M}^{-1}$), the decay of CuO_2^+ to either $Cu^+_{aq} + O_2$ or $Cu^{2+} + {}^{\cdot}O_2^-$ ($k_{-5}/k_{+7} = 81–89$) and the stability of $Cu(MeCN)_3^+$ ($\beta_3/\beta_2 = 1.5–2.1 \mathrm{M}^{-1}$). All these values can be observed also in the absence of Cu^{2+} and are quite independent of the data set and mechanism selected.

As mentioned above, the $1/[H^+]$ term based on (*8*) is at the border of significance based on the present results. In view of the data shown in *Fig. 3* and the specific influence on the relatively few experiments performed close to pH 5, we assume that such a term reflects some real reactivity. It seems at the same time reasonable that charge separation in the electron-transfer steps is supported by OH^-, and also that hydrolytic tendencies of Cu^I increase after oxygenation. In mechanistic schemes *b* and *c*, step (*8*) would have to be modified, however, and be replaced by (*8b*) and (*8c*).

$$CuO_2^+ + OH^- \underset{}{\overset{K_8}{\rightleftharpoons}} CuO_2(OH) \xrightarrow{k_{+8b}} Cu^{2+} + {}^{\cdot}O_2^-(+OH^-) \qquad (8b)$$

$$CuO_2(OH) + Cu^I_{tot} \xrightarrow{k_{+8c}, 2H^+} 2Cu^{2+} + H_2O_2(+OH^-) \qquad (8c)$$

In fact, as far as a $1/[H^+]$ term is considered real, we assume the expanded form (*8b*) and (*8c*) to represent the mechanistic steps for all three mechanisms discussed here.

The autoxidation of the simple solvated Cu^+ ion has to be described by a rather complicated mechanism, the elementary steps of which could be characterized by this comprehensive study in the presence of large excess of Cu^{II}. Competing one- and two-electron reduction is indispensable to account for the experimental data. Individual reactions of $HO_2^{\cdot}$ and $^{\cdot}O_2^-$ are extremely fast with Cu^I and Cu^{II}, and it has been unequivocally shown that the intermediates $HO_2^{\cdot}$, CuO_2^+ (and probably $^{\cdot}O_2^-$) hardly discriminate between Cu^+_{aq} and the various MeCN complexes in their reactivity.

Experimental. – $Cu(MeCN)_4BF_4$ was synthesized according to [33] and stored as a sat. soln. in pure MeCN. Stock solns. of the compound were standardized by spectrophotometric titration with EDTA in AcOH buffer after autoxidation to Cu^{2+}. MeCN, *p.A., Merck,* was kept dry by 3-Å molecular sieve. Other reagents were of anal. grade and used as obtained. pH was adjusted to the desired values using HNO_3 or buffers based on $Cl_2CHCOOH$, $ClCH_2COOH$, and CH_3COOH in combination with NaOH. All measurements were done at an ionic strength $I = 0.5$M (KNO_3) and a temp. of 298 ± 0.2 K.

Instrumentation. The consumption of O_2 was studied using an oxygen electrode with a setup described in [19] ($[O_2]$ was adjusted to roughly $5 \cdot 10^{-5}$M by bubbling with N_2). However, the output voltage was digitized on-line using an *AT 286* personal computer (*Plantroon*) equipped with a *PCL-714* multifunctional interface card, programmed to simulate a 10-Hz digital voltmeter. Digitized curves were evaluated by a modified version of initial rates: the first parts of the reaction curves (roughly 1/3 of total O_2 consumption) were evaluated by least-squares fitting with the exponential *Eqn. 14*. Based on the values of A_0, A_1, and k, initial rates $= -d[O_2]/dt$ and

$$[O_2] = A_0 + A_1e^{-kt} \tag{14}$$

$k_{obs} = -d[O_2]/(dt \cdot [O_2])$ were calculated for $t = 0$. With this approach, the exact calibration of the electrode does not affect the results as long as the response in millivolt is linear to $[O_2]$. This was checked daily. Final calculations based on rate laws derived from various mechanistic schemes were done with a general nonlinear least-squares program on a *HP 300* desk-top computer. The goodness of fit was estimated from the overall variances (*15*).

$$\sigma^2 = \sum_{i=1}^{I} \frac{(\log k_{obs}(i) - \log k_{calc}(i))^2}{I - n} \tag{15}$$

(I = number of data points, n = number of adjustable parameters).

Financial support of this work by the *Amt für Ausbildungsbeiträge,* Basel (personal grant to *L. M.*) and by the *Swiss National Science Foundation* (grant No. 20-27936.89) is gratefully acknowledged.

REFERENCES

[1] K. P. Balakrishnan, A. D. Zuberbühler, *Helv. Chim. Acta* **1984,** *67,* 2068.

[2] H. Gampp, A. D. Zuberbühler, in 'Metal Ions in Biological Systems', Ed. H. Sigel, Marcel Dekker, New York, 1981, Vol. 12, pp. 133–189.

[3] A. D. Zuberbühler, in 'Copper Coordination Chemistry', Eds. K. D. Karlin and J. Zubieta, Adenine, New York, 1983, pp. 237–258.

[4] Z. Tyeklár, K. D. Karlin, *Acc. Chem. Res.* **1989,** *22,* 241.

[5] A. D. Zuberbühler, in 'Dioxygen Activation and Homogeneous Catalytic Oxidation', Ed. L. I. Simándi, Elsevier, Amsterdam, 1991, pp. 249–257.

[6] H. Gampp, A. D. Zuberbühler, *Chimia* **1978,** *32,* 54.

[7] C. A. Sprecher, A. D. Zuberbühler, *Angew. Chem. Int. Ed.* **1977,** *16,* 189.

[8] E. V. Shtamm, Y. I. Skurlatov, *Russ. J. Phys. Chem.* **1974,** *48,* 852.

[9] E. V. Shtamm, A. P. Purmal, Y. I. Skurlatov, *Russ. J. Phys. Chem.* **1974,** *48,* 1320.

[10] Z. Szeverényi, U. Knopp, A. D. Zuberbühler, *Helv. Chim. Acta* **1982,** *65,* 2529.

[11] H. Gampp, D. Haspra, W. Spieler, A. D. Zuberbühler, *Helv. Chim. Acta* **1984,** *67,* 1019.

[12] J. Balla, T. Kiss, in 'Dioxygen Activation and Homogeneous Catalytic Oxidation', Ed. L. I. Simándi, Elsevier, Amsterdam, 1991, pp. 189–194.

[13] Z. Tyeklár, K. D. Karlin, in 'Dioxygen Activation and Homogeneous Catalytic Oxidation', Ed. L. I. Simándi, Elsevier, Amsterdam, 1991, pp. 237–248.

[14] E. V. Shtamm, A. P. Purmal, Y. I. Skurlatov, *Russ. J. Phys. Chem.* **1977,** *51,* 1829.

[15] V. M. Berdnikov, Y. N. Kozlov, A. P. Purmal, *Chim. Vys. Energ.* **1969,** *3,* 370.

[16] D. E. Cabelli, B. H. J. Bielski, J. Holcman, *J. Am. Chem. Soc.* **1987,** *109,* 3665.

[17] Y. N. Kozlov, V. M. Berdnikov, *Z. Fiz. Chim.* **1973,** *47,* 598.
[18] A. D. Zuberbühler, *Helv. Chim. Acta* **1976,** *59,* 1448.
[19] M. Güntensperger, A. D. Zuberbühler, *Helv. Chim. Acta* **1977,** *60,* 2584.
[20] H. J. Forman, I. Fridovich, *Arch. Biochem. Biophys.* **1973,** *158,* 396.
[21] R. D. Gray, *J. Am. Chem. Soc.* **1969,** *91,* 56.
[22] A. D. Zuberbühler, *Helv. Chim. Acta* **1970,** *53,* 473.
[23] A. Günter, A. D. Zuberbühler, *Chimia* **1970,** *24,* 340.
[24] P. Hemmerich, C. Sigwart, *Experientia* **1963,** *19,* 488.
[25] P. M. Henry, *Inorg. Chem.* **1966,** *5,* 688.
[26] G. Rainoni, A. D. Zuberbühler, *Chimia* **1974,** *28,* 67.
[27] K. D. Karlin, N. Wei, B. Jung, S. Kaderli, A. D. Zuberbühler, *J. Am. Chem. Soc.* **1991,** *113,* 5868.
[28] P. R. Bevington, in 'Data Reduction and Error Analysis for the Physical Sciences', McGraw-Hill, New York, 1969, pp. 317–323.
[29] B. H. J. Bielski, *Photochem. Photobiol.* **1978,** *28,* 645.
[30] D. Behar, G. Czapski, J. Rabani, L. M. Dorfman, H. A. Schwarz, *J. Phys. Chem.* **1970,** *74,* 3209.
[31] D. Klug, J. Rabani, *J. Biol. Chem.* **1972,** *247,* 4839.
[32] K. Sehested, O. L. Rasmussen, H. Fricke, *J. Phys. Chem.* **1968,** *72,* 626.
[33] Ger. Pat. No. 1230025, cited in *Chem. Abstr.* **1967,** *66,* 46487e.