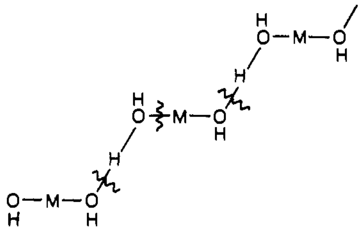

H bond has a bond energy of ~100 KJ).[5] Such an increase will prevent the olation of trans isomers at a temperature lower than the temperature at which total decomposition occurs (~250 °C).

Comparison and Correlation of Structure. The main difference between compounds **1** and **2** is in the way that the mononuclear hydroxoaqua species interact with each other. Structure **1** consists of chains of hydroxoaqua ions linked by a weaker, long [2.586 (6) Å], and asymmetric hydrogen bond between aqua and hydroxo ligands of neighboring chromium atoms (Figure 3).[7] The aqua and hydroxo ligands in this compound do *not* lose their identity and may be easily recognized by their very different Cr–O bond length [1.998 (5) and 1.926 (4) Å, respectively]. The two oxygen atoms of the hydroxo and aqua ligands of each chromium atom are also hydrogen bonded to two oxygen atoms of the dithionate counter ion as can be seen from Figure 3. This feature may account for the stabilization of this unusual hydroxoaqua structure in the crystalline state. Compound **1** provides the only example out of over 20 structures reported so far,[5] in which the hydroxo and aqua ligands of neighboring metal atoms do not merge into a symmetrical H_3O_2 ligand.

The replacement of the dithionate counter ion by iodide as in **2** is sufficient to change this unusual mode of interaction of $[Cr(pico)_2(H_2O)(OH)]^{2+}$ and convert it to a normal binuclear configuration with two $H_3O_2^-$ bridges.

The structure of the di-μ-$H_3O_2^-$ bridged dimer in **2** is similar to the one found in the iodide salt of *cis*-$[(bpy)_2Cr(H_3O_2)_2Cr(bpy)_2]^{4+}$.[5a,b] In both complexes the M–O···O–M bridges have torsional angles of an approximately gauche configuration as a result of the rigid double bridging system. From Table IV it can be seen that in **2** the two $H_3O_2^-$ bridges are not identical as in the bpy complex. The O···O separations are 2.50 (1) and 2.48 (1) Å and the torsional angles are 60.4° and 90.1°, respectively. In the bpy complex the O···O separation is shorter, 2.446 (5) Å, and the torsional angle is 64.9°. The distortion in **2** is probably the result of the difference in the hydrogen bonding to the $H_3O_2^-$ units or due to other lattice forces.

Acknowledgment. We are grateful to the Fund for Basic Research administered by the Israel Academy of Sciences and Humanities for financial support.

Supplementary Material Available: Tables of thermal parameters and positional parameters of hydrogen atoms of **2**, positional and thermal parameters and bond lengths and angles for **3** (9 pages). Ordering information is given on any current masthead page.

Kinetics and Mechanism of the Reaction of the Bis(1,10-phenanthroline)copper(I) Ion with Hydrogen Peroxide in Aqueous Solution

G. R. Alastair Johnson* and Najdat B. Nazhat

Contribution from the Laboratory of Radiation and Biophysical Chemistry, School of Chemistry, The University, Newcastle upon Tyne, England NE1 7RU. *Received August 4, 1986*

Abstract: Investigations of the reaction of the bis(1,10-phenanthroline)copper(I) ion, $Cu(phen)_2^+$, with hydrogen peroxide in the presence of a scavenger (RH = methanol, ethanol, 2-propanol, or formate ion) and of the reactions initiated by radiation-produced hydroxyl free radical, $OH^•$, in similar systems in the absence of H_2O_2 show that $OH^•$ is not formed by the $Cu(phen)_2^+ + H_2O_2$ reaction. The observed kinetics and stoichiometry of this reaction are interpreted in terms of a mechanism involving an intermediate, possibly a $Cu–H_2O_2$ complex, formed by reaction of $Cu(phen)_2^+$ with H_2O_2. The rate constant for the reaction of this intermediate with RH is smaller, by a factor of at least 10^4, than that for the reaction of $OH^•$ with RH.

The observation that cleavage of DNA is efficiently induced by treatment with 1,10-phenanthroline (phen), in the presence of H_2O_2, copper(II) ions, and various reducing agents[1-5] has stimulated interest in the mechanism of the reaction of $Cu(phen)_2^+$ with H_2O_2. It has usually been assumed[5-8] that the reactive intermediate is the hydroxyl free radical ($OH^•$), produced according to eq 1

$$Cu(phen)_2^+ + H_2O_2 \rightarrow Cu(phen)_2^{2+} + OH^• + OH^- \quad (1)$$

If $OH^•$ is involved, this should be apparent from the kinetics of the $Cu(phen)_2^+ + H_2O_2$ reaction, in the presence of an $OH^•$ scavenger, RH (e.g., an alcohol). Under these circumstances, generation of $OH^•$ by reaction 1 would be expected to lead to a chain reaction, because the free radical, $R^•$, produced by the scavenging reaction 2, is capable of reducing $Cu(phen)_2^{2+}$ by reaction 3 (where P is the oxidation product from $R^•$).

$$OH^• + RH \rightarrow R^• + H_2O \quad (2)$$

$$R^• + Cu(phen)_2^{2+} \rightarrow Cu(phen)_2^+ + P + H^+ \quad (3)$$

We recently investigated[9] the reaction of the aquacopper(I) ion with H_2O_2 with methanol as scavenger. In this case, reactions

---

(1) Sigman, D. S.; Graham, D. R.; D'Aurora, V.; Stern, A. M. *J. Biol. Chem.* **1979**, *254*, 2269.

(2) Que, B. G.; Doweny, K. M.; So, A. G. *Biochem.* **1980**, *19*, 5987.

(3) Marshall, L. E.; Graham, D. R.; Reich, K. A.; Sigman, D. S. *Biochem.* **1981**, *20*, 244.

(4) Reich, K. A.; Marshall, L. E.; Graham, D. R.; Sigman, D. S. *J. Am. Chem. Soc.* **1981**, *103*, 3582.

(5) Gutteridge, J. M.; Halliwell, B. *Biochem. Pharmacol.* **1982**, *31*, 2801.

(6) Goldstein, S.; Czapski, G. *J. Am. Chem. Soc.* **1983**, *105*, 7276.

(7) Goldstein, S.; Czapski, G. *Inorg. Chem.* **1985**, *24*, 1087.

(8) Goldstein, S.; Czapski, G. *J. Am. Chem. Soc.* **1986**, *108*, 2244.

(9) Johnson, G. R. A.; Nazhat, N. B.; Saadalla-Nazhat, R. A. *J. Chem. Soc., Chem. Commun.* **1985**, 407.

0002-7863/87/1509-1990$01.50/0

analogous to those represented by eq 1–3 constitute a chain reaction leading to methanol oxidation, the chain length of which can be predicted from the known rate constant values. The observed chain length was much shorter than predicted, and, furthermore, was inhibited by phen, indicating that $OH^{\bullet}$ is not produced by reaction of either the aqua- or the phen-complexed Cu^{I} ion with H_2O_2. Some published data, obtained in an investigation[6] of the reaction of H_2O_2 with $Cu(phen)_2^{+}$, produced by pulse radiolysis of $Cu(phen)_2^{2+}$ solutions, also indicated that $OH^{\bullet}$ is not an intermediate. In the pulse radiolysis experiments, formate ions were used to scavenge the radiation-produced $OH^{\bullet}$ and thereby generate the $CO_2^{\bullet-}$ radical that reduced $Cu(phen)_2^{2+}$ to $Cu(phen)_2^{+}$. Production of $OH^{\bullet}$ by reaction 1 under these conditions would be expected to lead to a chain oxidation of the formate ion by H_2O_2, with the copper complex acting as catalyst. Although the kinetics of $Cu(phen)_2^{+}$ disappearance were explained[6] in terms of reaction 1, there was no experimental indication of a chain reaction. Similarly, the results of a stopped-flow kinetic investigation of the $Cu(phen)_2^{+} + H_2O_2$ reaction were interpreted[10] in terms of a mechanism involving reaction 1, in spite of there being no chain decomposition of H_2O_2 in the presence of $OH^{\bullet}$ scavengers such as ethanol.

We have investigated the reactions of radiation-produced $OH^{\bullet}$ in solutions containing the Cu^{I} and Cu^{II} phen complexes and RH, in the absence of H_2O_2, in order to predict more precisely the kinetic behavior expected from the production of $OH^{\bullet}$ by reaction 1. It was confirmed that if reaction 1 occurred in the Cu(phen) + H_2O_2 + RH system, reactions 2 and 3 would also occur and would lead to a chain reaction for which the chain length can be predicted. It is shown that the kinetics and stoichiometry of the overall reaction observed in this system are not those expected if reaction 1 were involved, and an alternative mechanism is suggested.

Experimental Section

Materials. $Cu(phen)_2^{2+}$ was prepared by mixing stock solutions of copper(II) sulfate (BDH, A.R.) and 1,10-phenanthroline (BDH) at natural pH. $Cu(phen)_2^{+}$ was prepared either by adding solid copper(I) chloride to a deaerated solution of phen (0.01 M) or by γ-irradiation of a deaerated $Cu(phen)_2^{2+}$ solution ($1–2 \times 10^{-4}$ M) containing either methanol, ethanol, 2-propanol, or sodium formate (0.001 M).

Procedures. Solutions were prepared in 100-mL syringes, from which samples were transferred directly to 10-mL syringes for the experiments. Solutions were deaerated, as required, by bubbling with O_2-free N_2. The pH was adjusted with H_2SO_4, NaOH, or phosphate buffer.

A photodiode array spectrophotometer (Hewlett-Packard, HP8451A) was used for absorbance measurement. This was equipped with a flow cell into which solutions could be introduced directly from a syringe and which was also used as the detection cell in a stopped-flow apparatus in following the kinetics of the $Cu(phen)_2^{+} + H_2O_2$ reaction. In the latter case, the cell was filled, via thermostatted reservoirs and mixing chamber, from two separate syringes. Mixing of the two reactant solutions, one containing $Cu(phen)_2^{+}$ (+ $Cu(phen)_2^{2+}$), the other H_2O_2, with additives as required, was rapid compared to the instrument response time (0.1 s). The HP8451A microprocessor was used for data analysis.

Irradiations were carried out by using a Co-60 γ-ray source (nominally 800 Ci), with the solution held in a fixed position near to the source in either a syringe or a glass radiation vessel with a 1-cm path length quartz spectrophotometer cell attached via a graded seal. The solution in the radiation vessel was deaerated by pumping on a vacuum line before irradiation and closed by a high-vacuum stopcock. The dose rate, determined by Fricke dosimetry, was approximately 20 Gy min^{-1}.

H_2O_2 was determined by reduction of copper(II) ions in the presence of excess 2,9-dimethyl-1,10-phenanthroline (dmp). $Cu(dmp)_2^{+}$, formation of which is quantitative under the conditions used,[11] was measured spectrophotometrically ($\epsilon = 7500 \pm 300$ M^{-1} cm^{-1} at 454 nm, determined by using standard solutions prepared by reduction of $Cu(dmp)_2^{2+}$ with hydroxylamine).

Absorption Spectrum of $Cu(phen)_2^{+}$. For determination of ϵ_{max}, solutions of $Cu(phen)_2^{+}$ were prepared by reduction of the Cu^{II} complex with ascorbate: 5 mL of sodium ascorbate solution (0.01 M, pH 7) was mixed in a syringe with 5 mL of $Cu(phen)_2^{2+}$ solution (known concentration $<1.2 \times 10^{-4}$ M). Absorption spectra of $Cu(phen)_2^{+}$ solutions, prepared by the three methods described above, were measured at concentrations in the range used in the kinetic experiments ($<2 \times 10^{-5}$ M); the spectra of samples obtained by the different methods were indistinguishable. $\lambda_{max} = 430 \pm 2$ nm, $\epsilon_{430} = 5400 \pm 150$ M^{-1} cm^{-1}, independent of the ratio [phen]/[Cu] (2–5) and of $[Cu(phen)_2^{+}] = 0.5–5.0 \times 10^{-5}$ M. At higher concentrations, up to $[Cu(phen)_2^{+}] = 11.0 \times 10^{-5}$ M, ϵ_{max} was the same as at lower concentrations, but λ_{max} decreased slightly with increasing concentration to $\lambda_{max} = 410$ nm at the greatest concentration used. The effects of solutes ($Cu(phen)_2^{2+}$, phen, alcohols, and HCO_2^{-}) on the absorption spectrum were investigated by using a 10^{-5} M $Cu(phen)_2^{+}$ solution. No change in the spectrum was observed with $[Cu(phen)_2^{2+}] < 10^{-4}$ M. With added alcohols, there was no change in λ_{max}, but the ϵ_{max} increased slightly with increasing alcohol concentration, e.g., for 2-propanol (1.3 M) $\epsilon_{max} = 6300$ M^{-1} cm^{-1}. With HCO_2^{-}, there was a significant change in the spectrum, λ_{max} moving to shorter wavelengths, with a decrease in λ_{max}, dependent on HCO_2^{-} concentration ($\epsilon_{max} = 4950$, 4850 M^{-1} cm^{-1} at 0.05, 0.1 M HCO_2^{-}, respectively).

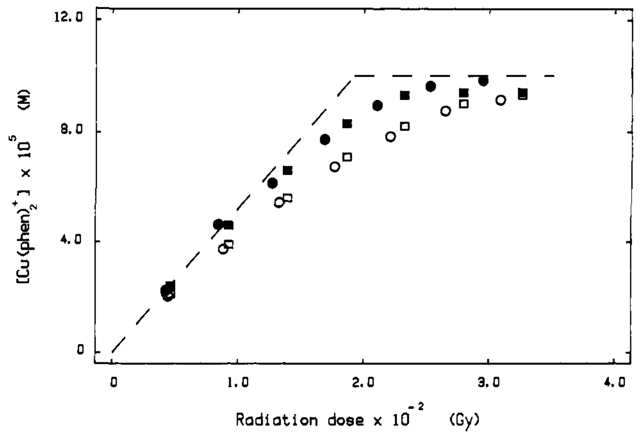

Figure 1. Formation of $Cu(phen)_2^{+}$ from $Cu(phen)_2^{2+}$ by γ-irradiation (N_2O saturated solutions) in presence of 0.1 M methanol (open points) and 2-propanol (filled points). Circles are measured; squares are calculated values; line calculated assuming no back-reaction (see text). Initial $[Cu(phen)_2^{2+}] = 1.0 \times 10^{-4}$ M.

Results

Reactions of $OH^{\bullet}$ in the Copper–Phenanthroline + RH System. γ-irradiation is a well-established method of generating free radicals. In N_2O-saturated aqueous solution this produces mainly $OH^{\bullet}$, together with smaller yields of hydrogen atoms ($H^{\bullet}$) and H_2O_2. At the solute concentrations used, the radiation yields[12] are $G(OH^{\bullet}) = 0.63$, $G(H^{\bullet}) = 0.063$, and $G(H_2O_2) = 0.083$ μmol J^{-1} (uncertainty of about 10%). We investigated the reactions initiated by radiation-produced $OH^{\bullet}$ in solutions containing $Cu(phen)_2^{+}$, $Cu(phen)_2^{2+}$, and RH (methanol, 2-propanol or formate ion; 0.1 M). The yield of the Cu^{I} complex was determined from the absorption spectrum, measured at intervals during irradiation, the exposure being interrupted for this purpose. In most of the experiments, the initial concentrations were $[Cu^{II}]_0 = 1.0 \times 10^{-4}$, $[phen]_0 = 2.1 \times 10^{-4}$ M), where it can be assumed that the bis complex is the major reacting species.[13] The spectrum at each dose used was indistinguishable from that of $Cu(phen)_2^{+}$, at the same concentration, prepared by the other methods (described in the Experimental Section). The radiation yield at the lowest dose used (42 Gy) was $G(Cu^{I}) = 0.52 \pm 0.03$ μmol J^{-1}, irrespective of the scavenger used. With RH = HCO_2^{-}, the radiation yield remained constant at this value until all of the Cu^{II} initially present was reduced to Cu^{I}. With RH = methanol or 2-propanol, the radiation yield decreased with increasing dose (Figure 1).

H_2O_2 + $Cu(phen)_2^{+}$ Reaction. A. Without Scavenging Solute. The kinetics of the $Cu(phen)_2^{+} + H_2O_2$ reaction were followed (298 K) by measurement of the $Cu(phen)_2^{+}$ absorbance at λ_{max} (430 nm) following rapid mixing of the reactant solutions, under

---

(10) Ponganis, K. V.; de Araujo, M. A.; Hodges, H. L. *Inorg. Chem.* **1980**, *19*, 2704.

(11) Davies, G.; Higgins, R.; Loose, D. J. *Inorg. Chem.* **1976**, *15*, 700.

(12) Buxton, G. V. *Radiation Res. Rev.* **1968**, *1*, 209.

(13) Yandell, J. K. In *Copper Coordination Chemistry: Biochemical and Inorganic* Perspectives; Karlin, K. D., Zubieta, J., Eds.; Adenine Press: New York, 1983; p 157.

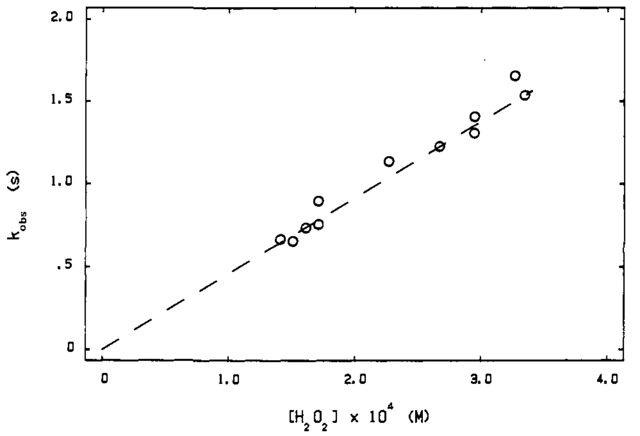

Figure 2. Reaction of $Cu(phen)_2^+$ with H_2O_2 in absence of scavenger. Dependence of first-order rate constant for disappearance of $Cu(phen)_2^+$, k_{obsd}, on H_2O_2 concentration. Initial $[Cu(phen)_2^+] = 1-8 \times 10^{-5}$ M, pH 3.7–9.0, 298 K.

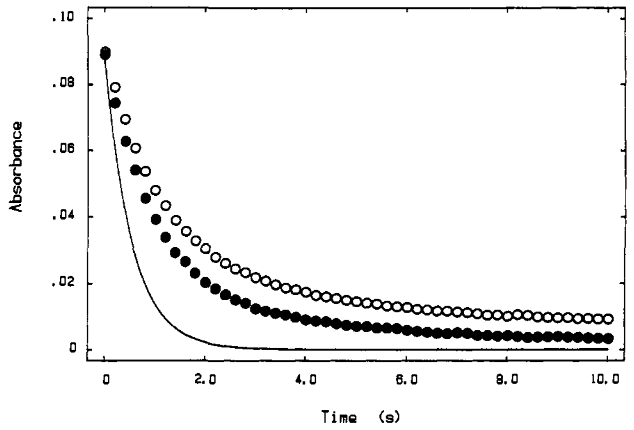

Figure 3. Reaction of $Cu(phen)_2^+$ with H_2O_2 in presence of 2-propanol. Dependence of absorbance (430 nm) on time. Filled and open points are measured values for 0.1 and 0.5 M 2-propanol, respectively. Line is calculated for reaction without scavenger (see text). Initial $[Cu(phen)_2^+] = 1.7 \times 10^{-5}$ M, $[H_2O_2] = 4.0 \times 10^{-4}$ M, pH 5.6, 298 K.

O_2-free conditions. At the initial reactant concentrations used, i.e., ($[Cu(phen)_2^+]_0 = 1-8 \times 10^{-5}$, $[H_2O_2]_0 = 1-3 \times 10^{-4}$ M), the H_2O_2 concentration change in the reaction was kinetically negligible. In most of the runs, the ratio $[Cu(phen)_2^{2+}]_0/[Cu(phen)^+]_0 \simeq 1$; increasing this ratio to 5 did not change the kinetics.

The disappearance of $Cu(phen)_2^+$ was first order in $Cu(phen)_2^+$ (i.e., $-d[Cu(phen)_2^+]/dt = k_{obsd}[Cu(phen)_2^+]$) and in H_2O_2, shown by the linear dependence of k_{obsd} on H_2O_2 concentration (Figure 2). The value of the second-order rate constant, $k_{obsd}/[H_2O_2] = 4.6 \pm 0.4 \times 10^3$ M^{-1} s^{-1}, is close to that previously reported.[10] At constant H_2O_2 concentration and with $[Cu(phen)_2^+]_0 = 5 \times 10^{-5}$ M, k_{obsd} was independent of pH (3.7–9.0) and of phen concentration (10^{-4}–10^{-3} M).

The stoichiometric ratio, $R_s = \Delta[H_2O_2]/\Delta[Cu(phen)_2^+]$ was measured by determining the decrease in H_2O_2 concentration on mixing known concentrations of $Cu(phen)_2^+$ and H_2O_2. The initial conditions were kept as close as possible to those used in the kinetic runs. Five independent determinations, with initial concentration ranges $[H_2O_2] = (1.7-3.5) \times 10^{-4}$, $[Cu(phen)_2^+] = (3-8) \times 10^{-5}$ M, gave $R_s = 0.6$ (standard deviation = 0.2).

B. With Scavenging Solute. Kinetic runs were carried out, with methanol, ethanol, 2-propanol, or formate as solute, for $[RH]_0 = (0.05-1.0)$ M. Initial $Cu(phen)_2^+$ and H_2O_2 concentrations were as in the absence of scavenger. No change in the kinetics was apparent on varying the pH (5.0–9.0) or the $Cu(phen)_2^{2+}$ concentration ($1-10 \times 10^{-5}$ M).

Typical kinetic plots, showing the effects of varying concentration of a particular scavenger (2-propanol) are shown in Figure 3. All of the scavengers investigated decreased the rate of $Cu(phen)_2^+$ disappearance, the extent of retardation increasing with scavenger concentration. At a given scavenger concentration, the retardation effect was similar for ethanol, 2-propanol, and formate ion but greater for each of these solutes than for methanol.

With methanol, ethanol, 2-propanol (1.0 M), or formate (0.1 M) present, the stoichiometric ratio $R_s = 1.5 \pm 0.5$ was measured by using the method described in the previous section.

Discussion

$OH^\bullet$ Reactions in the $Cu(phen)_2^+ + Cu(phen)_2^{2+} + RH$ System. In the systems under consideration, the main reactions of the radiation-produced radicals, $OH^\bullet$ and $H^\bullet$, are represented by eq 2 and 4. The radicals, $R^\bullet$, produced by these reactions can undergo reactions 3 and 5.

$$H^\bullet + RH \rightarrow R^\bullet + H_2 \qquad (4)$$

$$R^\bullet + Cu(phen)_2^+ \ (+ H^+) \rightarrow Cu(phen)_2^{2+} + RH \qquad (5)$$

At the concentrations used in the radiation experiments ($[RH]/[Cu(total)] \simeq 1000$, $[RH]/[phen] \simeq 500$), reaction 2 is fast compared with other possible reactions of $OH^\bullet$, with either phen or the copper complexes.[14] Similarly, reaction 4 is the predominant reaction of $H^\bullet$.[15] The free radical, $R^\bullet$, produced by reactions 2 and 4 is $CO_2^{\bullet-}$ ($RH = HCO_2^-$) or a 1-hydroxyalkyl radical (RH = methanol or ethanol). In the case of 2-propanol, reaction 2 gives mainly $(CH_3)_2C^\bullet(OH)$, with a small fraction (<10%) of $OH^\bullet$ reacting to give $CH_3CH(OH)CH_2^\bullet$.[16]

In the mechanism for the $Cu(phen)_2^+ + H_2O_2 + RH$ reaction that assumes reaction 1 to be the initiation step, reactions 3 and 5 are potentially propagation and termination steps, respectively; a knowledge of the relative rates of these reactions is, therefore, crucial in predicting the kinetic behavior from this mechanism. The required information about the rate constant ratio, k_3/k_5, was obtained from an analysis of the dose-dependence of the radiation yield of $Cu(phen)_2^+$ from $Cu(phen)_2^{2+}$ in the presence of a scavenger, RH (Figure 1).

At low conversions of Cu^{II} to Cu^I, where reaction 5 is negligible, the predicted net radiation yield of $Cu(phen)_2^+$ depends on the reaction of $Cu(phen)_2^+$ with H_2O_2, produced as a primary species, as well as on reactions 2–4. The occurrence of reaction 1, together with reactions 2–4, would imply a theoretical net radiation yield

$$G(Cu^I)_{initial} = G(OH^\bullet) + G(H^\bullet) = 0.69 \ \mu mol \ J^{-1}$$

If, however, the $Cu(phen)_2^+ + H_2O_2$ reaction occurs by a mechanism that results in a net loss of $Cu(phen)_2^+$, as suggested by our experiments with the $Cu(phen)_2^+ + H_2O_2$ reaction (discussed below), then $G(Cu^I)_{initial}$ depends on the stoichiometry of this H_2O_2 removal process. For [RH] = 0.1 M, with $[Cu(phen)_2^+] = 2 \times 10^{-5}$ M, the concentration at the lowest radiation dose used, our mechanism implies that approximately 2 molecules of $Cu(phen)_2^+$ would be lost for each molecule of H_2O_2 formed, giving

$$G(Cu^I)_{initial} = G(OH^\bullet) + G(H^\bullet) - 2G(H_2O_2) = 0.52 \ \mu mol \ J^{-1}$$

At the lowest dose, the observed yield was $G(Cu(phen)_2^+) = 0.52 \pm 0.03$ μmol J^{-1} (RH = methanol, 2-propanol, formate ion at 0.10 M), in agreement with this theoretical value.

With increasing radiation dose, as the ratio $[Cu(phen)_2^+]/[Cu(phen)_2^{2+}]$ increases, competition of reaction 5 with reaction

---

[14] $k_2 = 3, 2,$ and 0.9 ($\times 10^9$) M^{-1} s^{-1} for RH = formate, 2-propanol, and methanol, respectively (see: Dorfman, L. M.; Adams, G. E. *Reactivity of the Hydroxyl Radical in Aqueous Solution*; U.S. Government Printing Office: Washington, DC, 1972; NSRDS-NBS46); the alternative reactions cannot compete successfully even if diffusion-controlled.

[15] Reaction of $H^\bullet$ by addition to phen may occur to some extent with methanol as scavenger (taking k_4(RH = methanol) = 2×10^6 M^{-1} s^{-1} and k(H + phen) = 1×10^9 M^{-1} s^{-1}. This effect is too small to influence the main conclusions and, for the other scavengers, with $k_4 \geqslant 1 \times 10^7$ M^{-1} s^{-1}, reaction 4 will certainly predominate. (Rate constant values from Anbar, M.; Farhartaziz; Ross, A. B. *Selected Specific Rates of Reactions of Transients from Water in Aqueous Solution, II. Hydrogen Atom*; U.S. Government Printing Office: Washington, DC, 1975; NSRDS-NBS51).

[16] Anbar, M.; Meyerstein, D.; Neta, P. *J. Chem. Soc. B* **1966**, 742. Simic, M. G.; Hoffman, M. Z.; Brezniak, N. V. *J. Am. Chem. Soc.* **1977**, *99*, 2166.

3 becomes increasingly important, leading to a decrease in the radiation yield of $G(\mathrm{Cu(phen)_2^+})$ with increasing dose. At a sufficiently high total dose, a steady state is predicted, with a constant value of the ratio

$$([\mathrm{Cu(phen)_2^+}]/[\mathrm{Cu(phen)_2^{2+}}])_{ss} = S_r k_3/k_5$$

where $S_r = [G(\mathrm{OH^\bullet}) - 2G(\mathrm{H_2O_2})]/[G(\mathrm{OH^\bullet}) + 2G(\mathrm{H_2O_2})]$. In principle, therefore, the rate constant ratio, k_3/k_5, can be calculated from the measured value of $([\mathrm{Cu(phen)_2^+}]/[\mathrm{Cu(phen)_2^{2+}}])_{ss}$. With $\mathrm{RH = HCO_2^-}$, $\mathrm{Cu(phen)_2^{2+}}$ was reduced quantitatively to $\mathrm{Cu(phen)_2^+}$, and it can be concluded that reaction 5 is negligible at all stages of the reaction. With RH = methanol or 2-propanol, a steady state was reached at conversion of $\mathrm{Cu(phen)_2^{2+}}$ to $\mathrm{Cu(phen)_2^+}$ of about 95% (Figure 1). Because of the experimental uncertainties in the concentration measurements, this high converison meant that a precise value of the rate constant ratio could not be obtained, although it is possible to derive a lower limit. Taking $([\mathrm{Cu(phen)_2^+}]/[\mathrm{Cu(phen)_2^{2+}}])_{ss} \geqslant 20$, with $S_r = 0.6$, gives $k_3/k_5 \geqslant 30$.

As a further check that the results are consistent with the occurrence of reactions 2–5, the yield for a certain dose, in the approach to the steady state, was calculated, by using a numerical integration procedure[17] to model the reacting system (Figure 1). In the case of methanol, where only the one radical, $^\bullet\mathrm{CH_2OH}$, is involved, a value $k_3/k_5 = 30$ was assumed for the model. With 2-propanol, both the 1-hydroxyalkyl and 2-hydroxyalkyl radicals participate in reactions 3 and 5, and, to account for the slower approach to the steady state observed in this case, it was assumed that the ratio, k_3/k_5 is much lower for the 1-hydroxy than for the 2-hydroxy radical. The computed values for 2-propanol, shown in Figure 2, were obtained assuming that 10% of reacting radicals are 2-hydroxyalkyl and that k_3/k_5 for this species is 3000 times greater than that for the 1-hydroxyalkyl radical.

The conclusion that the radiation yields can be explained in terms of reactions 2–5 implies that reactions of $\mathrm{R^\bullet}$ with phen are negligible. This is not unexpected because reactions of C-centered radicals with aromatic compounds typically have rate constants that are small[18] compared with those for their oxidation by $\mathrm{Cu^{II}}$ ions.

The values we found for the relative rates of reactions 3 and 5 are in general agreement with the limited amount of information that is available concerning reactions of C-centered free radicals with copper ions. Except for $\mathrm{CO_2^{\bullet -}}$, for which $k_3 = 1.2 \times 10^9$ $\mathrm{M^{-1}\ s^{-1}}$ has been reported,[6] rate constant values for the reactions with phen complexed ions are not available. Some values have been reported for reactions analogous to reaction 3, involving oxidation of a 1-hydroxyalkyl radical by the aquacopper(II) ion,[19] viz., 16, 9, and 5 ($\times 10^7$) $\mathrm{M^{-1}\ s^{-1}}$ for $\mathrm{R^\bullet} = \bullet\mathrm{CH_2OH}$, $\mathrm{CH_3C^\bullet HOH}$, and $\mathrm{(CH_3)_2C^\bullet OH}$, respectively. There is also evidence[19,20] that $\mathrm{CO_2^{\bullet -}}$ and 1-hydroxyalkyl radicals do not react to oxidize the aquacopper(I) ion to copper(II), although 2-hydroxyalkyl radicals do react, by a process leading to oxidation of the metal ion and dehydration of the radical.[19]

The value of $([\mathrm{Cu(phen)_2^+}]/[\mathrm{Cu(phen)_2^{2+}}])_{ss}$, measured in radiation experiments, was dependent on the initial [phen]/[copper] ratio. Although values of the formation constants for the Cu(I) complexes are not available and the species concentrations are therefore unknown, with $[\mathrm{phen}]/[\mathrm{Cu^{II}}] < 2$ it is to be expected that both the mono and the bis copper complexes will be present. Under these conditions, the steady-state ratio, $\mathrm{Cu^I/Cu^{II}}$, was less than that with the stoichiometric ratio, $[\mathrm{phen}]/[\mathrm{Cu^{II}}] = 2$, and dependent both on the $[\mathrm{phen}]/[\mathrm{Cu^{II}}]$ ratio and on the particular $\mathrm{OH^\bullet}$ scavenger used. These results indicate that the ratio k_3/k_5 depends on the extent of complexing of the metal ions although it cannot be decided, on the basis of present evidence, whether this effect is attributable to the change in the complexing of $\mathrm{Cu^{II}}$, $\mathrm{Cu^I}$, or both. Our investigations of the $\mathrm{Cu(phen)_2^+ + H_2O_2}$ reaction were confined to conditions where it can be assumed that the bis complexes are the main copper species and that the k_3/k_5 ratio is that obtained from the radiation experiments.

The $\mathrm{Cu(phen)_2^+ + H_2O_2}$ + RH Reaction. A. Mechanism with $\mathrm{OH^\bullet}$ as Intermediate. In the $\mathrm{Cu(phen)_2^+ + H_2O_2}$ reaction in the absence of RH, $\mathrm{OH^\bullet}$ produced by reaction 1 would be expected to oxidize $\mathrm{Cu^I}$ according to eq 6

$$\mathrm{OH^\bullet + Cu(phen)_2^+ + (H^+) \rightarrow Cu(phen)_2^{2+} + H_2O} \quad (6)$$

Assuming reaction 6 to be fast compared with reaction 1, this would imply that the pseudo-first-order rate constant $k_{\mathrm{obsd}} = 2k_1$. In the presence of RH, taking into account the information available about the reactions of $\mathrm{OH^\bullet}$, discussed above, it can be concluded that production of $\mathrm{OH^\bullet}$ by reaction 1, in the presence of $\mathrm{Cu(phen)_2^{2+}}$ and RH, would initiate a chain reaction, propagated by reactions 1–3 with (for RH = methanol, ethanol, or 2-propanol) reaction 5 as the main termination step. (Reaction 2 is fast compared with reaction 6 under the conditions used). For this mechanism, the steady-state approximation gives eq 7

$$-\mathrm{d}[\mathrm{Cu^I}]/\mathrm{d}t = 2k_1k_5[\mathrm{Cu^I}]^2[\mathrm{H_2O_2}]/(k_3[\mathrm{Cu^{II}}] + k_5[\mathrm{Cu^I}]) \quad (7)$$

(where $\mathrm{Cu^I}$ and $\mathrm{Cu^{II}}$ represent the corresponding copper phen complexes).

For the experimental conditions used in the kinetic experiments, i.e., with $[\mathrm{Cu(phen)_2^{2+}}]/[\mathrm{Cu(phen)_2^+}] > 1$, and taking $k_3/k_5 \geqslant 30$ (obtained from the γ-radiation experiments), eq 7 approximates to eq 8.

$$-\mathrm{d}[\mathrm{Cu^I}]/\mathrm{d}t = 2k_1k_5[\mathrm{Cu^I}]^2[\mathrm{H_2O_2}]/k_3[\mathrm{Cu^{II}}] \quad (8)$$

This mechanism predicts, therefore, a reaction rate independent of RH concentration and decreasing with increasing $\mathrm{Cu(phen)_2^{2+}}$ concentration. Also, according to this mechanism, with $[\mathrm{Cu(phen)_2^{2+}}] > [\mathrm{Cu(phen)_2^+}]$, the decay of $\mathrm{Cu(phen)_2^+}$ should be approximately second order in $\mathrm{Cu(phen)_2^+}$, with an observed rate constant equal to $2k_1k_5[\mathrm{H_2O_2}]/k_3[\mathrm{Cu(phen)_2^{2+}}]$. Under the experimental conditions used to obtain the data in Figure 3, for example, this implies an upper limit of about 600 $\mathrm{M^{-1}\ s^{-1}}$ for the value of second-order constant (taking $k_1 = 2 \times 10^3 \mathrm{M^{-1}\ s^{-1}}$), i.e., a first half-life of at least 100 s for the decay of $\mathrm{Cu(phen)_2^+}$. With formate ion as scavenger, reaction 5 does not occur, and the most probable termination reaction is the radical–radical reaction 9

$$\mathrm{2CO_2^- \rightarrow HCOO^- + CO_2} \quad (9)$$

In this case, therefore, a significantly longer chain would be expected, implying an even slower decay of $\mathrm{Cu(phen)_2^+}$ than that predicted for an alcohol as scavenger.

The experimental kinetic data are clearly not in agreement with these predictions. The observed rate of decay of $\mathrm{Cu(phen)_2^+}$ is independent of $\mathrm{Cu(phen)_2^{2+}}$ concentration, dependent on RH concentration, and much faster than predicted (e.g., first half-life <2 s, [RH] = 0.5 M, Figure 3).

The disagreement between the $\mathrm{OH^\bullet}$ mechanism and the experimental findings is also apparent from the value of the stoichiometric ratio, $R_s = \Delta[\mathrm{H_2O_2}]/\Delta[\mathrm{Cu(phen)_2^+}]$, which, according to this mechanism, is approximately equal to the chain length. This gives a predicted lower limit, $R_s = k_3[\mathrm{Cu(phen)_2^{2+}}]/k_5[\mathrm{Cu(phen)_2^+}] \geqslant 30$, i.e., significantly greater than the observed value, $R_s \simeq 1.5$.

In the discussion so far, we have tacitly assumed homogeneous distribution of the free radicals. It is necessary, however, to consider the possibility that $\mathrm{OH^\bullet}$, produced by reaction 1, reacts preferentially with a ligand of the $\mathrm{Cu(phen)_2^{2+}}$ present in the same solvent cage. This type of reaction has been discussed for $\mathrm{H_2O_2}$ decomposition catalyzed by iron(II) complexes.[21] It is evident that such a solvent cage reaction would generate a ligand free

---

[17] Chance, E. M.; Curtis, A. R.; Jones, I. P.; Kirby, C. R. Facsimile, U. K. *Atomic Energy Authority*; Harwell: 1977.

[18] Neta, P. *Adv. Phys. Org. Chem.* **1976**, *12*, 223.

[19] Buxton, G. V.; Green, J. C. *J. Chem. Soc., Faraday Trans. 1* **1978**, *74*, 697.

[20] Das, S.; Johnson, G. R. A. *J. Chem. Soc., Faraday Trans. 1* **1980**, *76*, 1779.

[21] Walling, C.; Amarnath, K. *J. Am. Chem. Soc.* **1982**, *104*, 1185. We thank one of the referees for drawing this to our attention.

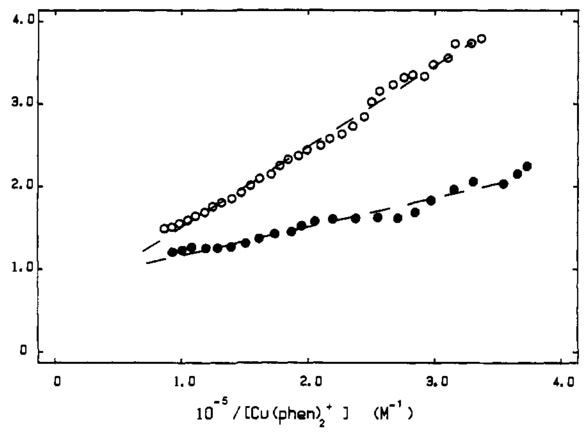

Figure 4. Reaction of $Cu(phen)_2^+$ with H_2O_2 in presence of 2-propanol. Kinetic data (Figure 3) plotted according to eq 13 (see text). Filled and open points are measured values for 0.1 and 0.5 M 2-propanol, respectively. Initial $[Cu(phen)_2^+] = 1.7 \times 10^{-5}$ M, $[H_2O_2] = 4.0 \times 10^{-4}$ M.

radical that, in turn, would undergo reactions analogous to reactions 3 and 5. The observed stoichiometry and kinetics, in the absence of RH, are not consistent with participation of ligand radicals, and we consider there is no evidence for $OH^\bullet$ reactions with ligands in the systems investigated.

B. An Alternative Mechanism. The experimental observations can be explained if an intermediate is produced by the $Cu(phen)_2^+$ + H_2O_2 reaction that reacts much more slowly than $OH^\bullet$ with RH, allowing reaction of the intermediate with $Cu(phen)_2^+$ to compete favorably with its scavenging by RH. The mechanism is represented schematically by eq 10–12 (where $Cu(H_2O_2)$ represents the intermediate), together with reaction 3. (The approximation is made here, that reaction 5 is negligible compared with reaction 3.

$$Cu^{I} + H_2O_2 \rightarrow Cu(H_2O_2) \qquad (10)$$

$$Cu(H_2O_2) + RH \rightarrow R^\bullet + Cu^{II} + OH^- + H_2O \qquad (11)$$

$$Cu(H_2O_2) + Cu^{I} \rightarrow 2Cu^{II} + 2OH^- \qquad (12)$$

For this mechanism, assuming reaction 10 to be slow compared with reaction 12, the pseudo-first-order rate constant $k_{obsd} = 2k_{10}$, giving $k_{10} = (2.3 \pm 0.2) \times 10^3\ M^{-1}\ s^{-1}$.

This mechanism can account for the observed kinetics in the presence of RH, including the dependence of the reaction rate on RH concentration. Equation 13 is derived from this mechanism, by using the steady-state approximation

$$2[Cu(phen)_2^+][H_2O_2]/R_t = 1/k_{10} + k_{11}[RH]/k_{10}k_{12}[Cu(phen)_2^+] \qquad (13)$$

where $R_t = -d[Cu(phen)_2^+]/dt$. The experimental data were analyzed, by using the HP8451A derivative routine to evaluate R_t, with the approximation that the H_2O_2 concentration is constant and equal to the initial value. Plots of $[Cu(phen)_2^+]/R_t$ against $1/[Cu(phen)_2^+]$ were linear, in accordance with eq 13, as shown in Figure 4, with the data from Figure 3. The least-squares slopes gave values of the ratio k_{11}/k_{12} equal to $(4 \pm 2) \times 10^{-5}$ (RH = 2-propanol, ethanol, formate), and $(8 \pm 4) \times 10^{-6}$ (RH = methanol). These ratios were calculated taking $k_{10} = 2.3 \times 10^3\ M^{-1}\ s^{-1}$, i.e., the value measured in the absence of RH; values of k_{10} obtained from intercepts of the derivative plots at $1/[Cu(phen)_2^+] = 0$ agreed with this value, within experimental uncertainty.

It can be assumed that $k_{12} \leq 10^{10}\ M^{-1}\ s^{-1}$, the estimated diffusion-controlled value.[22] The measured ratio, k_{11}/k_{12}, therefore, implies an upper limit for the rate constant for the reaction of the intermediate with RH, $k_{11} \leq 4 \times 10^5\ M^{-1}\ s^{-1}$ (RH = 2-propanol). This is much smaller than the rate constant for the reaction of $OH^\bullet$ with 2-propanol, $k_2 = 2 \times 10^9\ M^{-1}\ s^{-1}$ (ref 14).

Nature of the Intermediate. The possibility that an intermediate other than $OH^\bullet$ is involved in copper-catalyzed H_2O_2 reactions has been the subject of earlier discussion, and, although references to this hypothetical intermediate as "crypto-OH" are indicative of the lack of any precise knowledge, there has been speculation that either cupryl ($Cu(OH)^{2+}$) or a complex of H_2O_2 with copper(I) may be involved.[23-26] There is spectroscopic and kinetic evidence for mixed ternary Cu(II) complexes, containing H_2O_2 as one of the ligands.[27] Presumably, in the case of Cu(I) where coordination numbers greater than 4 are unusual, only one bidentate ligand will remain bound, together with H_2O_2, in a mixed complex. Depending on the extent of electron transfer, within the complex, the resulting species can be regarded as either Cu(I) with coordinated H_2O_2, Cu(II) with coordinated $OH^\bullet$ and OH^-, i.e., $(phen)Cu^{II}(OH^\bullet,OH^-)$, or Cu(III) with coordinated OH^-, i.e., $(phen)Cu^{III}(OH^-)_2$. Our kinetic data show the intermediate from the $Cu(phen)_2^+ + H_2O_2$ reaction can dehydrogenate RH but with a much lower specific rate than the corresponding $OH^\bullet$ reaction. This behavior, although providing no certain information about the structure of the intermediate, indicates perhaps that it is most closely approximated as $OH^\bullet$ coordinated to Cu^{II}. The aquacopper(I) ion reacts with H_2O_2 to give an intermediate that shows a pH-dependence in its reactions,[9] and it was suggested that this intermediate may be the same as a species, produced by reaction of $OH^\bullet$ with aquacopper(II) ions, which is believed to be an aquacopper(III) complex, existing with different extents of protonation, depending on the pH value.[28] It is, perhaps, significant that there is no indication of any pH-dependence in the reactions of the intermediate produced from the phen-complexed ion.

The conclusion, from the present investigation, that reaction of the intermediate from the $Cu(phen)_2^+ + H_2O_2$ reaction with $Cu(phen)_2^+$ to give $Cu(phen)_2^{2+}$ is fast, with a rate constant about 10^5 times greater than that for its reaction with organic solutes, taken together with the relatively slow specific rate of the $Cu(phen)_2^+ + H_2O_2$ reaction implies a low stationary concentration of the intermediate under all conditions, making its direct detection impracticable.

Registry No. $Cu(phen)_2^+$, 17378-82-4; H_2O_2, 7722-84-1; MeOH, 67-56-1; EtOH, 64-17-5; *i*-PrOH, 67-63-0; HCO_2^-, 71-47-6.

---

(22) Weston, R. E.; Schwartz, H. A. *Chemical Kinetics*; Prentice Hall: 1972; p 158.

(23) Aust, S. D.; Morehouse, L. A.; Thomas, C. E. *J. Free Radicals Biol. Med.* **1985**, *1*, 3.

(24) Gorbunova, N. V.; Purmal, A. P.; Skurlatov, Yu. I. *Russ. J. Phys. Chem. (Engl. Transl.)* **1975**, 5987.

(25) Czapski, G.; Aronovitch, J.; Samuni, A.; Chevion, M. In *Oxyradicals and Their Scavenger Systems. Molecular Aspects*; Cohen, G., Greenwald, R. A., Eds.; Elsevier; 1983, Vol. 1, p 111.

(26) Sawyer, D. T. in ref 25, p 134.

(27) Sigel, H.; Flierl, C.; Griesser, R. *J. Am. Chem. Soc.* **1969**, *91*, 1061.

(28) Asmus, K. D.; Bonifacic, M.; O'Neill, P.; Schulte-Frohlinde, D.; Steenken, S.; Toffel, P. *J. Chem. Soc., Faraday Trans. 1*, **1978**, *74*, 1820.