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Reactions of Low-Valent Transition-Metal Complexes with Hydrogen Peroxide. Are They "Fenton-like" or Not? 1. The Case of Cu^+_{aq} and Cr^{2+}_{aq}

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Abstract: A thermodynamic analysis of the Fenton reaction and the "Fenton-like" reactions points out that their detailed mechanisms involve the formation of a transient complex between the low-valent cation $ML_m{}^n$ and hydrogen peroxide of the type $ML_{m-1}{}^n\cdot O_2H^-$. This complex might decompose into $ML_m{}^{n+1}$ + $^{\bullet}OH$ or $ML_m{}^{n+2}$ + H_2O or react directly with a substrate. Experimental data from studies in acidified solutions indicate that $(H_2O)_5Cr^{2+}\cdot O_2H^-$ decomposes into $Cr(H_2O)_6{}^{3+}$ + $^{\bullet}OH$ in the presence of $\geqslant$0.1 M ethanol, 2-propanol, and 2-butanol, whereas $(H_2O)_mCu^+\cdot O_2H^-$ reacts with the alcohols directly. However, in the absence of an organic substrate, the latter complex in acidic solution decomposes into $Cu(H_2O)_n{}^{2+}$ + $^{\bullet}OH$. The specific overall reaction rates of Cu^+_{aq} with H_2O_2, $(CH_3)_3COOH$, and $S_2O_8{}^{2-}$ are 4.1×10^3, $\sim 4 \times 10^3$, and $\geqslant 1 \times 10^7$ $M^{-1}\ s^{-1}$, respectively.

The oxidation of a variety of organic substrates by a mixture of a low-valent transition-metal complex and hydrogen peroxide is commonly attributed to a "Fenton-like" mechanism,[2-5] i.e.

$$ML_m{}^n + H_2O_2 \rightarrow ML_m{}^{n+1} + {}^{\bullet}OH + OH^- \qquad (1)$$

followed by eq 2 or 3.

$$^{\bullet}OH + RH \rightarrow {}^{\bullet}R + H_2O \qquad (2)$$

$$^{\bullet}OH + R_1R_2C{=}CR_3R_4 \rightarrow {}^{\bullet}CR_1R_2CR_3R_4(OH) \qquad (3)$$

This mechanism is of major importance owing to its role in many catalytic oxidations,[6,7] and it has been proposed as a key step in many biochemical processes.[8,9] Thus the toxicity of $O_2{}^{\bullet-}$ and other reductants in the presence of copper ions at pH ~7 has been attributed to the hydroxyl radicals formed in reaction 1.[10-15] The fact that relatively high concentrations of hydroxyl radical scavengers do not always protect the system has been attributed to a "site specific" mechanism, i.e., the metal ion is bound near the biological target and the damage is caused by the hydroxyl free radical immediately after its formation.[10-18]

Recent studies of the reactions of H_2O_2 with Cu^+_{aq},[19] $Cu(phen)_2{}^+$,[20] $Cu(bpy)_2{}^+$,[21] polyaminocarboxylate complexes of iron(II),[22] $U(IV)_{aq}$,[23] and $Ru(Hedta)H_2O$[24] indicated that at least under some conditions free hydroxyl radicals are not formed and that reaction 1 does not represent accurately the chemistry involved. It was suggested[19] that H_2O_2 oxidizes Cu^+_{aq} directly to Cu^{III}_{aq}, eq 4. The suggestion was based on the discrepancy[25]

$$Cu^+_{aq} + H_2O_2 \xrightarrow{2H^+} Cu^{III}_{aq} + 2H_2O \qquad (4)$$

between the experimental yields of CH_2O in γ-irradiated solutions containing Cu^{2+}_{aq}, H_2O_2, and CH_3OH and those calculated under the assumption that the reaction takes place by the chain mechanism shown in eq 5-8.

$$^{\bullet}CH_2OH + Cu^{2+}_{aq} \rightarrow CH_2O + H_3O^+ + Cu^+_{aq} \qquad (5)$$

$$Cu^+_{aq} + H_2O_2 \rightarrow Cu^{2+}_{aq} + OH^- + {}^{\bullet}OH \text{ (or reaction 4)} \qquad (6)$$

$$^{\bullet}OH + CH_3OH \rightarrow H_2O + {}^{\bullet}CH_2OH \qquad (7)$$

$$Cu^{III}_{aq} + CH_3OH \rightarrow Cu^{2+}_{aq} + {}^{\bullet}CH_2OH + H^+ \qquad (8)$$

The authors, however, neglected reaction 9[26] which is shifted to

$$Cu^{III}_{aq} \rightleftharpoons Cu^{2+}_{aq} + {}^{\bullet}OH + H^+ \qquad (9)$$

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the right[27] in acidic solutions, as well as the observation that the oxidation of methanol by Cu^{III}_{aq} occurs by reactions 9 and 7.[26]

This study presents a thermodynamic analysis of reaction 1 and also provides new experimental data on the reactions of Cr^{2+}_{aq} and Cu^{+}_{aq} with H_2O_2 in the presence of organic substrates at low pH. The products of these reactions indicate the involvement of the free hydroxyl radicals in the oxidation of Cr^{2+}_{aq}, but not of Cu^{+}_{aq}.

Several values of the rate constant for the reaction of Cu^{+}_{aq} with H_2O_2 are available in the literature.[27-29] Our extrapolation of the data obtained in the presence of phenanthroline[27] to [phen] = 0 yields the rate constant $k_{Cu} < 500\ M^{-1}\ s^{-1}$ at pH 5.8. In a study of the photocatalytic decomposition of H_2O_2 in the presence of copper ions the value $k_{Cu} = 4.7 \times 10^3\ M^{-1}\ s^{-1}$ at pH 2.3 was obtained,[28] whereas a recent book gives a value of $10^9\ M^{-1}\ s^{-1}$.[29] In view of the large discrepancy between the published reports we studied the kinetics of the oxidation of Cu^{+}_{aq} by H_2O_2 by a direct measurement. The reactions with t-BuOOH and $S_2O_8^{2-}$ were also studied briefly.

Thermodynamics of the "Fenton-like" Reactions. The reduction potential for reaction 10 is 0.87 V at pH 0.0 and 0.46 V at pH 7.0.[30] Therefore the Gibbs free energy change in reaction 11 is

$$H_2O_2 + H_3O^+_{aq} + e^- \rightarrow {}^{\bullet}OH + 2H_2O \qquad (10)$$

$$ML_m^{\,n} + H_2O_2 + H_3O^+_{aq} \rightarrow ML_m^{\,n+1} + {}^{\bullet}OH + 2H_2O \qquad (11)$$

$0.87 - E_M^0$ V at pH 0.0 and $0.46 - E_M^0$ V at pH 7.0, where E_M^0 is the reduction potential for the $ML_m^{\,n+1}/ML_m^{\,n}$ couple at the pH stated. Equation 11 is, however, a sum of several consecutive reactions.

If it is assumed that the electron-transfer step, reaction 12, occurs by an outer-sphere mechanism, then the reactions to be considered are

$$ML_m^{\,n+} + H_2O_2 \rightarrow ML_m^{\,n+1} + H_2O_2^- \qquad (12)$$

$$H_2O_2^- \rightarrow {}^{\bullet}OH + OH^-_{aq} \qquad (13)$$

$$OH^-_{aq} + H_3O^+_{aq} \rightarrow 2H_2O \qquad (14)$$

Reaction 14 is exothermic by 19.6 and 9.5 kcal/mol at pH 0 and 7.0, respectively. Reaction 13 is also highly exothermic and reaction 12 endothermic because (as pointed out by a referee) the electron affinity of hydrogen peroxide is positive.

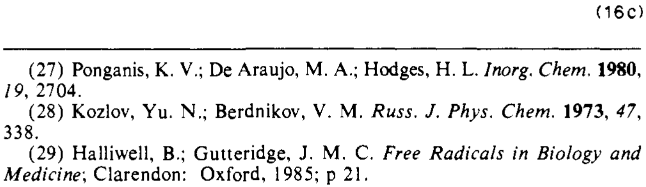
It is therefore unlikely that the "Fenton-like" processes occur by an outer-sphere mechanism. (Indeed, even $Ru(NH_3)_6^{2+}$ reduces H_2O_2 in an inner-sphere reaction.[31]) The first step is probably best represented by one of the reactions shown in eq 15a–c. In the following discussion we shall assume that the transient complex is $ML_{m-1}^{\,n}\cdot O_2H^-$, although the other two possibilities are equally valid.

$$ML_m^{\,n} + H_2O_2 \rightarrow ML_m^{\,n}\cdot H_2O_2 \qquad (15a)$$

$$\xrightarrow{\text{or}} ML_{m-1}^{\,n}\cdot O_2H^- + H_3O^+ + L \qquad (15b)$$

$$\xrightarrow{\text{or}} ML_m^{\,n}\cdot O_2H^- + H_3O^+ \qquad (15c)$$

The transient complex may decompose in one of the following reactions:



$$ML_{m-1}^{\,n}\,{}^{\bullet}O_2H^- \xrightarrow{+L+H_3O^+/H_2O} ML_m^{\,n+1} + {}^{\bullet}OH + H_2O/OH^-_{aq} \qquad (16a)$$

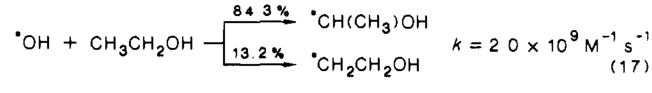
$$ML_{m-1}^{\,n}\,{}^{\bullet}O_2H^- \xrightarrow{+L+H_3O^+/H_2O} ML_m^{\,n+2} + H_2O/OH^-_{aq} \qquad (16b)$$

$$ML_{m-1}^{\,n}\,{}^{\bullet}O_2H^- \xrightarrow{+L+RH+H_3O^+/H_2O} ML_m^{\,n+1} + {}^{\bullet}R + H_2O/OH^-_{aq} \qquad (16c)$$

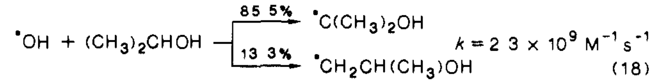
RH represents an aliphatic substrate as in reaction 2. Alternatively, an olefin might react with the transient complex in analogy to reaction 3. The ligand L in reaction 16 is usually a solvent molecule. The fate of the transient complex will depend on the relative rates of the three pathways for its decomposition, i.e., on the properties of $ML_m^{\,n}$ and RH and on the concentration of the latter. Thus the short chain length in the reduction of H_2O_2 by Cu^{+}_{aq}/CH_3OH is presently the only experimental evidence on which the formation of ${}^{\bullet}OH$ radicals has been ruled out. We therefore decided to check whether hydroxyl radicals are formed in the reactions of Cr^{2+}_{aq} and Cu^{+}_{aq} with H_2O_2 by analyzing the final products in the two systems.

Results and Discussion

Hydroxyl radicals react with ethanol and 2-propanol to yield the strongly reducing α-hydroxyalkyl radicals and weakly reducing β-hydroxyalkyl radicals in a ~6:1 ratio, eq 17 and 18.[32] It is reasonable to expect that this ratio will be different if the alcohols are oxidized by ${}^{\bullet}OH$, by $ML_{m-1}^{\,n}\cdot O_2H^-$ or by $ML_m^{\,n+2}$. Several studies were carried out in order to determine this ratio in different systems.[33-38] However, the results are not conclusive owing to the large difference in the chemical properties of the α and β free radicals, and their relative rates of reaction with $ML_m^{\,n}$ and $ML_m^{\,n+1}$.[3]



$${}^{\bullet}OH + CH_3CH_2OH \xrightarrow{84\ 3\%} {}^{\bullet}CH(CH_3)OH;\quad \xrightarrow{13.2\%} {}^{\bullet}CH_2CH_2OH \qquad k = 2\ 0 \times 10^9\ M^{-1}\ s^{-1} \qquad (17)$$



$${}^{\bullet}OH + (CH_3)_2CHOH \xrightarrow{85\ 5\%} {}^{\bullet}C(CH_3)_2OH;\quad \xrightarrow{13\ 3\%} {}^{\bullet}CH_2CH(CH_3)OH \qquad k = 2\ 3 \times 10^9\ M^{-1}\ s^{-1} \qquad (18)$$

We decided to overcome this difficulty by measuring the ratio $[{}^{\bullet}CH_2CH_2OH]/[{}^{\bullet}CH_2CH(CH_3)OH]$ formed in solutions containing ethanol and 2-propanol in equal concentrations. The chemical properties of the latter two radicals are similar and therefore slight changes in the $[ML_m^{\,n}]/[ML_m^{\,n+1}]$ ratio are not expected to affect the results. This point has to be checked experimentally.

The free radicals ${}^{\bullet}CH_2CHROH$, R = H or CH_3, react with Cr^{2+}_{aq}[39,40] and Cu^{+}_{aq}[38,41] to yield ethylene and propylene, eq 19 and 20. The specific rate of reaction of ${}^{\bullet}CH_2CH_2OH$ with Cr^{2+}_{aq} is $2.3 \times 10^8\ M^{-1}\ s^{-1}$.[40] The corresponding rate constant for the reaction of ${}^{\bullet}CH_2CH(CH_3)OH$ is expected to be similar.[42] These radicals are expected to react very slowly with Cr^{3+}_{aq}.[43] Therefore the ratio of ethylene to propylene in a solution containing Cr^{2+}_{aq} ions, ethanol, and 2-propanol equals the ratio of ${}^{\bullet}CH_2CH_2OH$ and ${}^{\bullet}CH_2CH(CH_3)OH$ formed in the solution.

$$M^n_{aq} + {}^{\bullet}CH_2CHROH \rightarrow [M^{n+1}{-}CH_2CHROH]^n \qquad (19)$$

$$[M^{n+1}{-}CH_2CHROH]^n \rightarrow M^{n+1}_{aq} + CH_2{=}CHR + OH^-_{aq} \qquad (20)$$

Solutions containing $[CH_3CH_2OH] = [(CH_3)_2CHOH]$ at $[ROH]_{tot} = 0.75$ M and 1.0×10^{-2} M Cr^{2+}_{aq} at pH 1.0 and 3.0

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Table I. Relative Yields of Propylene and Ethylene in the Reactions of Cu^+_{aq} and Cr^{2+}_{aq} with H_2O_2 in the Presence of Equimolar Amounts of 2-Propanol and Ethanol at pH 1[a]

$10^4[Cu^+_{aq}]$	$10^2[Cu^{2+}_{aq}]$	$10^4[H_2O_2]$	C_3H_6/C_2H_4[b]
5.0	1.0	8.0	7.8[c]
5.0	1.0	8.0	8.0
5.0	1.0	8.0	7.3[d]
5.0	1.0	8.0	8.3
5.0	2.0	8.0	8.2
5.0	3.0	8.0	8.0
5.0	1.0	10	8.0
5.0	1.0	20	7.8
5.0	2.0	8.0	7.9[e]
5.0	0.50		2.2[f]
5.0	1.0		2.2[f]
5.0	1.5		2.2[f]
5.0	2.0		2.2[f]
$10^2\ [Cr^{2+}_{aq}]$			
1.0		150	2.5
0.50		150	2.6
0.50		100	2.5
1.0		150	2.6
1.0		150	2.0[e]
0.3			2.3[f]
0.5			2.4[f]
1.0			2.9[f]
0.10			2.2[e,f]
0.30			2.0[e,f]

[a] Concentrations in mol dm^{-3}. Total alcohol concentration is [ROH] = 0.75 M. [b] Accuracy ±10%. [c] [ROH] = 0.25 M. [d] [ROH] = 0.5 M. [e] pH 3. [f] By radiation.

were mixed with deaerated H_2O_2, so that $[H_2O_2] = 1 \times 10^{-3}$ M. The ratios of propylene to ethylene formed are summarized in Table I. Identical solutions of Cr^{2+} in the absence of H_2O_2 were irradiated in a ^{60}Co γ-source and analyzed for propylene and ethylene. These results are also shown in Table I.

In the irradiated solutions the reactions 17–27 have to be considered. The relative yields of the products in reaction 21 are 2.65, 0.60, 2.65, 0.45, 0.75, and 2.65, respectively.[44]

$$H_2O \xrightarrow{\gamma,e^-} e^-_{aq},\ H^\bullet,\ OH^\bullet,\ H_2,\ H_2O_2,\ H_3O^+ \tag{21}$$

$$e^-_{aq} + Cr^{2+}_{aq} \rightarrow Cr^+_{aq} \qquad k = 1.4 \times 10^{10}\ M^{-1}\ s^{-1\,45} \tag{22}$$

$$Cr^+_{aq} + H_2O \xrightarrow{2H^+} Cr^{3+}_{aq} + H_2 \qquad k \leq 5 \times 10^3\ s^{-1\,45} \tag{23}$$

$$e^-_{aq} + H_3O^+ \rightarrow H^\bullet \qquad k = 2.3 \times 10^{10}\ M^{-1}\ s^{-1\,44} \tag{24}$$

$$H^\bullet + Cr^{2+}_{aq} \rightarrow CrH^{2+} \qquad k = 1.5 \times 10^9\ M^{-1}\ s^{-1\,45} \tag{25}$$

$$CrH^{2+}_{aq} + H_3O^+ \rightarrow Cr^{3+}_{aq} + H_2 \qquad k = 1.8 \times 10^4\ M^{-1}\ s^{-1\,45} \tag{26}$$

$$H^\bullet + CH_3CHROH \rightarrow {}^\bullet CR(CH_3)OH + {}^\bullet CH_2CHROH + H_2 \tag{27}$$

$$R = H,\ k_{27} = 2.5 \times 10^7\ M^{-1}\ s^{-1\,46}$$

$$R = CH_3,\ k_{27} = 1.8 \times 10^8\ M^{-1}\ s^{-1\,46}$$

At pH 3.0 reaction 22 competes effectively with reaction 24 and therefore the majority of the aliphatic radicals are formed in reactions 17 and 18. The observation that the ratios $[CH_3CH{=}CH_2]/[CH_2{=}CH_2]$ in the irradiated samples and in those mixed with H_2O_2 are equal shows that OH radicals are formed in the latter system, i.e., that $(H_2O)_5Cr^{III}{\cdot}O_2H^-$ decomposes as in eq 16a.

Table II. Relative Yields of 1-Butene and 2-Butene in the Reaction of Cu^+_{aq} with H_2O_2 in the Presence of 0.5 M 2-Butanol at pH 1[a]

$10^4[Cu^+_{aq}]$	$10^4[H_2O_2]$	1-butene/2-butene
5.0	8.0	0.35[b]
5.0	8.0	0.31
5.0	8.0	0.32[c]
5.0		0.05[d]
5.0		0.03[c,d]
2.0	10	0.28
5.0	10	0.29
8.0	10	0.31
5.0	8.0	0.28
5.0	8.0	0.30[e]
5.0	10	0.33
5.0	10	0.29[f]
5.0	10	0.33
5.0	40	0.27
5.0	80	0.32

[a] Concentrations in mol dm^{-3}. All the experiments had $[Cu^{2+}]$ = 0.01 M. [b] pH 3. [c] pH 0. [d] By radiation. [e] $[Cu^{2+}]$ = 0.02 M. [f] [2-Butanol] = 1 M.

At pH 1.0 all the hydrated electrons formed in the irradiated sample react as in eq 24. The fate of the hydrogen atoms depends on the competition between reactions 25 and 27. At high concentrations of Cr^{2+}_{aq} most of the hydrogen atoms react with it and therefore the majority of the aliphatic radicals are formed by reactions 17 and 18. Therefore the observation that the ratios $[CH_3CH{=}CH_2]/[CH_2{=}CH_2]$ are identical, within the experimental accuracy, for the irradiated samples and those to which H_2O_2 was added, shows also that free hydroxyl radicals are formed at this pH in the decomposition of $(H_2O)_5Cr^{III}{\cdot}O_2H^-$.[47]

The study was repeated with mixtures of Cu^+_{aq} and Cu^{2+}_{aq}. In these solutions the ${}^\bullet CR(CH_3)OH$ radicals reduce Cu^{2+}_{aq} to Cu^+_{aq}. The radicals ${}^\bullet CH_2CHROH$ react with Cu^+_{aq} to yield $Cu^{II}–CH_2CHROH$; the specific rates of the latter reactions are ~4 × $10^9\ M^{-1}\ s^{-1}$.[48] These complexes decompose to Cu^{2+}_{aq} and $CH_2{=}CHR$.[38,41] The radicals ${}^\bullet CH_2CHROH$ react also with Cu^{2+}_{aq}, the rate constant for ${}^\bullet CH_2CH_2OH$ being $3 \times 10^7\ M^{-1}\ s^{-1}$.[49] The reaction with ${}^\bullet CH_2CH(CH_3)OH$ is expected to proceed with a similar rate constant and to yield Cu^+_{aq} and the epoxide CH_2OCHR.[37,38] The relative yield of propylene and ethylene might therefore depend on the ratio $[Cu^+_{aq}]/[Cu^{2+}_{aq}]$ if a significant fraction of the free radicals react with Cu^{2+}_{aq}. The data in Table I indicate that the latter competition does not affect the results[50] under our experimental conditions.

In the samples irradiated in the ^{60}Co source the propylene to ethylene ratio is identical, within experimental accuracy, with that observed in the solutions containing low concentrations of Cr^{2+}_{aq}. This is in accord with expectations as Cu^{2+}_{aq} reacts with hydrogen atoms very slowly, $k < 10^6\ M^{-1}\ s^{-1}$,[49] and $[Cu^+_{aq}] < 1 \times 10^{-3}$ M. Therefore the majority of the H atoms react in reaction 27 in analogy to the solutions containing Cr^{2+}. These results show that the relative yields of the organic products do not depend on the nature of M^n_{aq} participating in reactions 19 and 20 as long as the concentration of M^{n+1}_{aq} is not too high.

Addition of H_2O_2 to a solution containing Cu^+_{aq}, Cu^{2+}_{aq}, and equal concentrations of ethanol and 2-propanol results in a ratio of propylene to ethylene that is considerably higher than that observed in the irradiated samples. The ratio is independent of the $[Cu^+_{aq}]/[Cu^{2+}_{aq}]$ ratio, the absolute concentration of the alcohols, and the pH (Table I). This result strongly indicates that the oxidation of Cu^+ by H_2O_2 does not proceed by the Fenton mechanism. The two-electron oxidation of Cu^+_{aq}, eq 4, is also

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(44) Matheson, M.; Dorfman, L. M. *Pulse Radiolysis*; MIT Press: Cambridge, MA, 1969.

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(46) Anbar, M.; Farhataziz, Ross A. B. *National Standard Reference Data System*; U.S. National Bureau of Standards: Washington, D.C., 1975; NBS-NSRDS, No. 51.

(47) The reason for the small change in the propylene to ethylene ratio with pH is unclear.

(48) The reactions of a series of aliphatic free radicals with Cu^+_{aq} have such rate constants, see, for example, Cohen and Meyerstein (Cohen, H.; Meyerstein, D. *Inorg. Chem.* **1986**, *25*, 1505) and results to be published.

(49) Freiberg, M.; Meyerstein, D. *J. Chem. Soc., Faraday Trans. 1* **1980**, *76*, 1825.

(50) Furthermore, no evidence for the formation of CH_2OCHR was obtained in the GC analysis.

ruled out as a major path, since the oxidation of alcohols by Cu^{III}_{aq} has reaction 9 as the first step.[26] It is therefore concluded that the reaction of Cu^+_{aq} with H_2O_2 yields $Cu^+{\cdot}O_2H^-$ which reacts with alcohols as in eq 16c.

In order to check the results, a second set of experiments was carried out. The mixture of 2-propanol and ethanol was replaced by 2-butanol. Hydrogen abstraction from 2-butanol yields a mixture of four free radicals, eq 28. The major product is expected to be III which is a strong reducing agent and is expected to reduce

$$\begin{aligned}&{}^{\bullet}OH + CH_3CH_2CH(OH)CH_3 \rightarrow \\ &\quad \{\underset{I}{{}^{\bullet}CH_2CH_2CH(OH)CH_3} + \underset{II}{CH_3\dot{C}HCH(OH)CH_3} + \\ &\quad \underset{III}{CH_3CH_2\dot{C}(OH)CH_3} + \underset{IV}{CH_3CH_2CH(OH)\dot{C}H_2}\} + H_2O \qquad (28)\end{aligned}$$

Cu^{2+}_{aq} even in the presence of Cu^+_{aq}.[41] In acidic solutions radical I is expected to oxidize Cu^+_{aq} and regenerate 2-butanol in analogy to the reaction of ${}^{\bullet}CH_3$.[48] Radicals II and IV are expected to react slowly with Cu^{2+}_{aq} and rapidly with Cu^+_{aq} followed by β-elimination of OH^-_{aq} and formation of $CH_3CH{=}CHCH_3$ and $CH_3CH_2CH{=}CH_2$, respectively. We measured the relative yields of the latter two products (Table II). In the irradiated solutions the ratio $[CH_2{=}CHC_2H_5]/[CH_3CH{=}CHCH_3]$ is 0.04 ± 0.01, similar to the ratio observed in solutions containing Cr^{2+}_{aq}.[40] In the mixtures with H_2O_2 the ratio is 0.31 ± 0.03. This result also indicates that hydroxyl radicals are not intermediates in the reaction of Cu^+_{aq} with H_2O_2.

Instead, the results suggest that $Cu^+{\cdot}O_2H^-$ is the major intermediate. Its lifetime is long enough for it to react with high concentrations of alcohols ($\geq$0.1 M). In view of the existence of this intermediate, the detailed mechanism[10,15,51] of the "Fenton-like" reactions involving copper ions has to be reconsidered. It is reasonable to assume that similar intermediates play an important role in other systems as was indicated in several cases.[19-24] Even for the reaction of Fe^{2+}_{aq} and H_2O_2 in nonaqueous solutions it was suggested that no free hydroxyl radicals are formed.[52]

The kinetics of the reactions of Cu^+_{aq} with H_2O_2 were determined under pseudo-first-order conditions. One series of experiments employed a large excess of H_2O_2. The pseudo-first-order rate constant k_{obsd} is proportional to $[H_2O_2]$. The plot passes through the origin and has a slope of $(8.5 \pm 0.2) \times 10^3$ M^{-1} s^{-1}. These determinations included a modest variation of $[H^+]$, 0.005–0.015 M, which had no effect over this concentration range.

With reversed concentrations, the plot of k_{obsd} versus $[Cu^+_{aq}]$ is also linear and has a slope of $(3.9 \pm 0.2) \times 10^3$ M^{-1} s^{-1}. Such experiments were necessarily carried out at lower concentrations, since the UV absorption of Cu^+_{aq} is the quantity being monitored in the run.

The two sets of experiments can be consolidated, as shown in Figure 1, which depicts simultaneously the variation of k_{obsd} against $2 \times [H_2O_2]$ and against $[Cu^+_{aq}]$. Within experimental error the points fall on the same line. Its slope, designated k_{29}, is $(4.1 \pm 0.4) \times 10^3$ M^{-1} s^{-1}.

The comparison between the alternative excess reagents amounts in effect to a kinetic determination of the stoichiometry of the net reaction, eq 29. The rate law is given by eq 30.

$$2Cu^+_{aq} + H_2O_2 + 2H^+ \rightarrow 2Cu^{2+}_{aq} + 2H_2O \qquad (29)$$

$$-d[H_2O_2]/dt = -d[Cu^+_{aq}]/2dt = k_{29}[Cu^+_{aq}][H_2O_2] \qquad (30)$$

Kinetics experiments using excess H_2O_2 were also performed with added 1 M *tert*-butyl alcohol. The plot of k_{obsd} against $[H_2O_2]$ is linear, but the rate constant, $(3.8 \pm 0.2) \times 10^3$ M^{-1} s^{-1}, is smaller than that found in the absence of the alcohol by a factor of 2.2 ± 0.2. The kinetic effect of *tert*-butyl alcohol cannot be explained solely by its role as a scavenger for either OH radicals or $Cu^+{\cdot}O_2H^-$, eq 2 or 16c ($R = HOC(CH_3)_2CH_2{}^{\bullet}$), since the *tert*-butyl alcohol radical itself reacts rapidly with Cu^+_{aq}, eq 31, $k = 2.6 \times 10^{10}$.[38] The effect of olefin, produced in eq 31, on the kinetics of reaction 29 has not been explored.

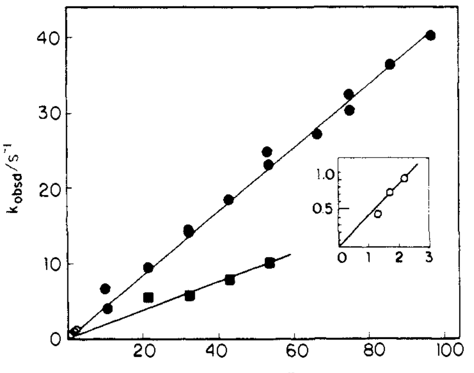

Figure 1. The pseudo-first-order rate constant for the reaction between Cu^+_{aq} and H_2O_2 varies linearly with the concentration of the reagent in excess. Data are shown for excess H_2O_2 (filled circles) and excess Cu^+ (open circles). Provided proper allowance is made for the stoichiometric factor of 2, then the data define a single straight line. (For clarity, some points near the origin are shown in the inset, in which a line with the same least-squares slope is drawn.) The rate constant decreases by a factor of 2 in the presence of 1 M *tert*-butyl alcohol (squares).

$$Cu^+_{aq} + HOC(CH_3)_2CH_2{}^{\bullet} \rightarrow Cu^{2+}_{aq} + CH_2{=}C(CH_3)_2 + OH^- \qquad (31)$$

The value of the rate constant k_{29} is considerably different from the lowest[27] and highest[29] literature values and agrees well with the rate constant obtained[28] by the rotating sector method in solutions containing Cu^{2+}_{aq} and H_2O_2 but no organic solute. The proposed chain mechanism in the latter study[28] has reaction 6 as one of the propagating steps. On the basis of the agreement between the directly measured rate constant k_{29} (4.1×10^3 M^{-1} s^{-1}) and that obtained indirectly in ref 28 (4.7×10^3 M^{-1} s^{-1}), one could conclude that reaction 6 is indeed a propagation step under the conditions reported.[28] Thus the experimental observations point out that the complex $(H_2O)_mCu^+{\cdot}O_2H^-$, formed in the reaction between Cu^+_{aq} and H_2O_2, reacts with alcohols in high concentration to form aliphatic free radicals. Hydroxyl free radicals are not involved except in the absence of an organic substrate where this complex decomposes into Cu^{2+}_{aq} + ${}^{\bullet}OH$.

The specific rates determined here are for the overall reaction 29. The primary step is reaction 15 followed by the reaction of $Cu^+{\cdot}O_2H^-_{aq}$ with another Cu^+_{aq}. Reaction 15 might, however, be an equilibrium reaction in which case the specific rates observed might depend on the experimental conditions and the value of K_{15}.

For comparison we also measured the specific rates of reaction of Cu^+_{aq} with $(CH_3)_3COOH$ and $S_2O_8^{2-}$. For *tert*-butyl hydroperoxide the kinetic data followed the pattern for hydrogen peroxide in major respects. k_{obsd} varies linearly with [*t*-BuOOH] and with $[Cu^+_{aq}]$ in the suitable experiments at pH 1. In a quantitative sense, however, the analysis is not as satisfactory. The slope of k_{obsd} versus [*t*-BuOOH] is $(5.6 \pm 0.1) \times 10^3$ M^{-1} s^{-1}, but in the reversed concentration experiments the slope versus $[Cu^+_{aq}]$ drops to only 4.2×10^3 M^{-} s^{-1}. It may be that side reactions with aliphatic radicals are more prevalent here (including perhaps the partial regeneration of Cu^+_{aq} after the reaction of ${}^{\bullet}CH_3$ with Cu^+_{aq} or Cu^{2+}_{aq}); if so, the idealized stoichiometry may be modified. Indeed GC analysis indicates that $[CH_4]:[C_2H_6] \simeq 2:1$. This suggests that both paths for $CuCH_3^+$ loss (acidolysis and bimolecular formation of ethane)[48] compete at pH ~1 under our experimental conditions. The rate constant for the *t*-BuOOH reaction that is analogous to k_{29} is $\sim 4 \times 10^3$ M^{-1} s^{-1}.

Peroxodisulfate Ions. The reaction between Cu^+_{aq} and $S_2O_8^{2-}$ was very rapid. Only at the very lowest concentrations could anything but a completed reaction be observed. The accumulation of 20 stopped-flow kinetic traces at very low and nearly equivalent concentrations gave $k \sim 10^{7.1}$ M^{-1} s^{-1}. Although this estimate seems valid, the difficulties with the experiments, including the

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use of an air-sensitive reagent at low concentration, are considerable. We cannot be confident of its reliability; we can, however, confidently state that persulfate reacts *much* more rapidly with Cu^+_{aq} than H_2O_2 and *t*-BuOOH do.

The latter result is somewhat surprising. Thus, for example, the specific rates of reaction of Cr^{2+}_{aq} with $S_2O_8^{2-}$, H_2O_2, and *t*-BuOOH are 2.5×10^4,[53] 7×10^4,[54] and 1.6×10^4 M^{-1} s^{-1}.[55] An inner-sphere mechanism was proposed for all three reactions. It is possible that Cu^+_{aq} reacts with $S_2O_8^{2-}$ by an outer-sphere mechanism.

Experimental Section

Peroxides were determined iodometrically; anaerobic conditions were required for precise results. Solutions of Cu^+_{aq} were prepared by reaction of Cr^{2+}_{aq} (from Cr^{3+}_{aq} on zinc amalgam and from Cr metal with acid) with excess Cu^{2+}_{aq}.[56] The concentrations of Cr^{2+}_{aq} were determined from the absorbance at 713 nm taking $\epsilon = 5$ M^{-1} cm^{-1}. The reaction medium contained only perchlorate ions, supplied by perchloric acid and lithium perchlorate. Ionic strength was not always maintained constant.

Kinetic data were determined at 25 °C by the stopped-flow technique with use of a Durrum-Gibson stopped-flow spectrophotometer interfaced with an OLIS 3820 data acquisition and analysis system. The data from every experiment followed pseudo-first-order kinetics and the rate constants were evaluated by standard methods. The values given are the average of six replicate determinations with any given set of solutions.

Hydrocarbon products were determined with Varian 3700 and Hewlett Packard 5790 chromatographs, calibrated with all the necessary standards. Prior to the analysis of olefins formed in solutions containing Cu^+_{aq}, an excess of $Fe_2(SO_4)_3$ was added. This is required in order to decrease the solubility of the olefins which form stable complexes with Cu^+_{aq}. All experiments were carried out anaerobically with Cr^{2+} or V^{2+}-scrubbed argon or nitrogen.

Irradiations were performed with a ^{60}Co γ-source with a dose rate of ca. 2.5×10^3 Gray/h or by a series of pulses from the linear electron accelerator of the Hebrew University of Jerusalem.

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Registry No. H_2O_2, 7722-84-1; Cu^+, 17493-86-6; Cr^{2+}, 22541-79-3; CH_3CH_2OH, 64-17-5; $(CH_3)_2CHOH$, 67-63-0; $CH_3CH_2CH(CH_3)OH$, 78-92-2; *t*-BuOOH, 110-05-4; $S_2O_8^{2-}$, 15092-81-6.

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Aroylnitrenes with Singlet Ground States: Photochemistry of Acetyl-Substituted Aroyl and Aryloxycarbonyl Azides

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Abstract: The photochemistry of 4-acetylbenzoyl azide (ABA), 4-acetyl-4′-biphenoyl azide (ADA), and 4-acetylphenoxycarbonyl azide (APA) shows unusual wavelength and structural effects. Irradiation of ABA or ADA into their π–π^* bands with deep-UV light leads to formation of 4-acetylbenzoylnitrene (ABN) and 4-acetyl-4′-biphenoylnitrene (ADN), respectively, in competition with photo-Curtius rearrangement to form isocyanates. Irradiation of these azides into their n–π^* bands with near-UV light gives only the aroylnitrenes. The triplet excited states of the azides were detected chemically and by transient spectroscopic techniques. Nitrogen loss following near-UV irradiation occurs exclusively from the excited triplet azides. However, the chemical properties of ABN and ADN are consistent only with reactions originating from their singlet states. An ESR spectrum is observed at 8 K for ((4-acetylphenoxy)carbonyl)nitrene (APN) but not for 4-acetylbenzoylnitrene (ABN) or 4-acetyl-4′-biphenylcarbonylnitrene (ADN). The chemical properties of APN in *tert*-butyl alcohol show that its triplet is no more than 5 kcal/mol below its lowest single state. In contrast, the chemical properties of ABN and ADN indicate that these nitrenes have singlet ground states.

Photochemical reactions of organic azides are specially important because of their use in lithography and in affinity labeling of biological macromolecules.[1,2] It is often assumed in these applications that irradiation of an aryl azide (ArN_3) generates an intermediate nitrene (ArN) which then plays the key role by determining the outcome of the reaction. For example, photolyses of the aryl diazides used in lithography is believed to give triplet nitrenes which crosslink a Novolac resin to modify its solubility properties.[3] Similarly, irradiation of nitro-substituted aryl azides, commonly used photolabeling agents, causes loss of nitrogen and, in favorable cases, formation of a covalent bond between the label and the targeted macromolecule.[4] The critical requirement for the intermediate in these applications is high chemical reactivity with a wide range of substrates. This is particularly true in a photolabeling experiment where the chemical composition of the target site is unknown.

All of the arylnitrenes that have been investigated to date have triplet ground states.[5] This is unfortunate with respect to applications since singlet nitrenes are generally much more reactive than are triplets. Indeed, we recently concluded that the triplet nitrenes formed from irradiation of nitro-substituted aryl azides may be of only modest utility in photolabeling experiments.[6]

Irradiation of aroyl azides ($ArCON_3$) or aryloxycarbonyl azides ($ArOCON_3$) leads to loss of nitrogen with formation of the corresponding nitrene (ArCON or ArOCON, respectively) and,

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