Oxidation of Copper(I)–Olefin Complexes in Aqueous Solution by Oxygen and Hydrogen Peroxide

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The absorption spectra and formation constants of the complexes of Cu^I with ethylene, isobutene, acrylamide, and allyl alcohol have been measured in aqueous solution. The oxidation of the allyl alcohol and ethylene complexes by O_2 and H_2O_2 has been investigated. In the former case H_2O_2 is a major product, and in the latter epoxide is formed. Reaction mechanisms which account for the observed kinetics and stoicheiometries are discussed.

ALTHOUGH the simple aqua-ion $Cu^+(aq)$ is not stable in aqueous solution it complexes strongly with olefins, and relatively stable solutions of these complexes can be prepared[1-4] under anaerobic conditions. Copper(I) complexed with either inorganic or organic ligands is rapidly oxidised by molecular oxygen and several mechanistic studies have been reported.[5-11] In some cases hydrogen peroxide has been shown to be a product. No study of the mechanism of oxidation of copper(I)–olefin complexes by O_2 has been reported, but such a study is of interest because of its relevance to the catalytic oxidation of olefins.

We report here the oxidation of copper(I)–allyl alcohol and –ethylene complexes by O_2 and H_2O_2. We also report absorption spectra and formation constants of some copper(I)–olefin complexes since these data are pertinent to the present study.

EXPERIMENTAL

A ^{60}Co γ-ray source providing a dose rate in the range 2—5 krad min^{-1} was used to irradiate the solutions.† A stopped-flow apparatus combined with an SP 700 recording spectrophotometer was used for measuring kinetics. This system was adequate for the study of reactions having a half-life > 5 s. For the kinetic measurements, solutions were irradiated in 10-cm^3 glass syringes, and for spectral measurements in conventional cells[12] having a side-arm sealed with a serum cap. Solutions were deaerated by bubbling with argon, or by evacuation, as appropriate. Details of the pulse-radiolysis apparatus and procedure have been described elsewhere.[13]

Allyl alcohol (Hopkin and Williams, G.P.R. grade) was dried over $Ca[SO_4]$ (24 h), distilled, and the middle fraction (b.p. 96—97 °C) collected. Methanol was either B.D.H. AnalaR grade which was dried, distilled, and the middle fraction collected, or B.D.H. Aristar grade which was used as supplied. Copper(II) salts were $Cu[SO_4]\cdot 7H_2O$ or $Cu[ClO_4]_2\cdot 6H_2O$ (B.D.H. AnalaR grade). Acrylamide (B.D.H. reagent grade) was recrystallised from dichloromethane and dried *in vacuo*. Hydrogen peroxide was B.D.H. reagent grade '40-volume' solution. Oxygen (B.O.C.) was taken straight from the cylinder. Ethylene (B.O.C.) and isobutene (Matheson) were condensed in a trap at −196 °C and uncondensed gas was pumped off. All the other reagents were B.D.H. AnalaR grade. The pH of the solutions was adjusted with $HClO_4$ or H_2SO_4.

Hydrogen peroxide was determined by the pertitanic acid method,[14] and solutions of Cu^{2+} were standardised by addition of excess of KI and back titration with thiosulphate. Ethylene oxide was determined by vapour-phase chromatography using a 9-ft column of 10% Carbo-

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† 1 rad = 10^{-2} J kg^{-1}; 1 eV ≈ 1.60×10^{-19} J.

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wax 1500 at 350 K. This method allowed concentrations $\geqslant 10^{-4}$ mol dm^{-3} to be measured. 2,3-Epoxypropen-1-ol was determined qualitatively by thin-layer chromatography. It was extracted into chloroform, concentrated by evaporation to 50 µl, and then applied to a 0.5-mm thick layer of Merck silica gel G. The sample and reference samples were eluted with chloroform and the spots were developed by charring with concentrated H_2SO_4 followed by heating over a gentle flame.

RESULTS

Production and Spectra of Copper(I)*–Olefin Complexes*.—The ion $Cu^+(aq)$ was generated by the radiolysis of deaerated solutions of $Cu^{2+}(aq)$ containing 1 mol dm^{-3} methanol. Under these conditions reactions (1)—(6) occur.[4] Thus $G(Cu^+) = G[e^-(aq)] + G(H) + G(OH)$ where $G(X)$ is the number of molecules of X produced per 100 eV

$$H_2O \rightsquigarrow e^-(aq),\ H,\ OH,\ H_2O_2, H_2 \quad (1)$$

$$e^-(aq) + Cu^{2+} \longrightarrow Cu^+ \quad (2)$$

$$H + Cu^{2+} \longrightarrow Cu^+ + H^+ \quad (3)$$

$$OH \text{ or } H + MeOH \longrightarrow \cdot CH_2OH + H_2O \text{ or } H_2 \quad (4)$$

$$\cdot CH_2OH + Cu^{2+} \longrightarrow Cu^+ + CH_2O + H^+ \quad (5)$$

$$Cu^+ + H_2O_2 \longrightarrow Cu^{2+} + OH + OH^- \quad (6)$$

of absorbed energy. The precise values of $G(X)$ are somewhat dependent on the solute concentrations.[15] Here we take $G[e^-(aq)] = G(OH) = 2.7$, $G(H) = 0.6$, and $G(H_2O_2) = 0.7$, values which are unlikely to be in error by more than 10%.

In the presence of olefin (L) reaction (7) occurs. Figure 1

$$Cu^+ + L \rightleftharpoons [Cu^IL] \quad (7)$$

shows that when an ethylene-saturated solution at pH 3 containing 9×10^{-4} mol dm^{-3} Cu^{2+} and 1 mol dm^{-3} methanol was γ-irradiated, the product copper(I)–ethylene complex accumulated at a constant rate until a dose of *ca.* 150 krad had been absorbed. No further product was formed at higher doses up to 400 krad. These observations are consistent with complete reduction of Cu^{2+} since a dose of 150 krad produces 9×10^{-4} mol dm^{-3} of X when $G(X) = 6$, which is the expected G value for Cu^+ as indicated above. They also show that the copper(I)–ethylene complex is not attacked by $e^-(aq)$, H, or $\cdot CH_2OH$ under the experimental conditions. Complexes of Cu^+ with acrylamide, isobutene, and allyl alcohol were produced in a similar manner, but in none of these cases were we able to achieve complete reduction of Cu^{2+}.

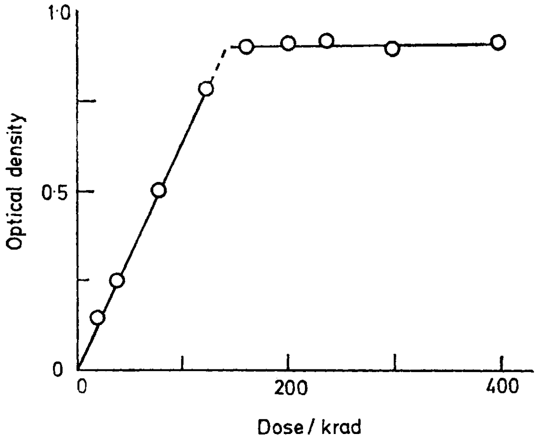

FIGURE 1 Increase in absorption of the copper(I) complex with dose (see text)

The spectra of the complexes are shown in Figure 2, and their absorption coefficients were obtained as described below. Since equilibrium (7) lies far to the right (see Table 1) for ethylene (L), $[Cu^IL]_\infty = [Cu^{2+}]_0$ and hence the absorption coefficient of $[Cu^IL]$ can be calculated. This method could not be used for the other complexes because the reduction of Cu^{2+} was not quantitative. Instead, the absorption coefficients of the other complexes were evaluated from the gradients of linear yield–dose plots by making the reasonable assumption that G[copper(I)–olefin] = G[copper(I)–ethylene] for solutions containing 1×10^{-2} mol dm^{-3} Cu^{2+}, 1 mol dm^{-3} methanol, and *ca.* 1×10^{-3} mol dm^{-3} olefin at pH 3. Under these conditions G[copper(I)–olefin] = 6.2, based on the absorption coefficient of the ethylene complex determined above.

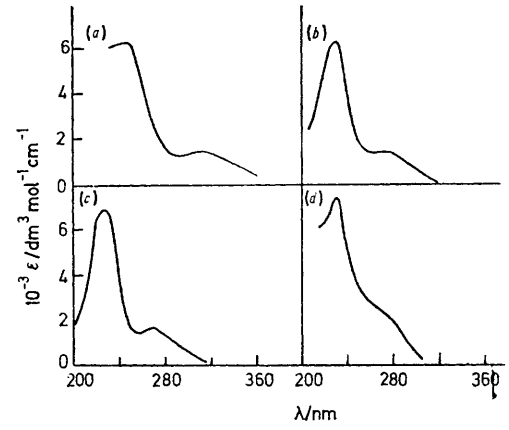

FIGURE 2 Absorption spectra of copper(I)–olefin complexes $[Cu^IL]$ in aqueous solution at pH 3. L = (*a*) Acrylamide, (*b*) allyl alcohol, (*c*) ethylene, and (*d*) isobutene

The spectra of the copper(I)–olefin complexes shown in Figure 2 are similar in shape and intensity to spectra of other such complexes in the literature.[2,4] They also show that conjugation in the olefin shifts the spectrum to longer wavelengths, a feature which has been noted before.[2]

TABLE 1

Absorption coefficients, $\varepsilon_{max.}$, and formation constants, K_7, of copper(I)–olefin complexes in aqueous solution at room temperature

Olefin	$\lambda_{max.}$/nm	$10^{-3}\varepsilon_{max.}$ [a] dm^3 mol^{-1} cm^{-1}	$10^{-4}K_7$ [a] dm^3 mol^{-1}
Acrylamide	250	6.2	2.1
	315	1.4	
Ethylene	228	6.8	22.2
	270	1.5	
Isobutene	230	7.4	2.7
	270 [b]	2.3	
Allyl alcohol	230	6.3	5.2 [c]
	270	1.5	

[a] ±5%. [b] Shoulder. [c] From ref. 1.

Formation Constants.—The formation constant of the

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[15] G. V. Buxton, *Radiation Res. Rev.*, 1968, **1**, 209.

copper(I)–acrylamide complex was obtained by pulse radiolysis of N_2O-saturated 1×10^{-2} mol dm^{-3} Cu^{2+} + 1 mol dm^{-3} methanol solution at pH 4 containing various concentrations of acrylamide. In this system reaction (8) occurs as well as (2), and the conditions employed ensured that reaction (9) could be neglected.[13] The amount of

$$e^-(aq) + N_2O \xrightarrow{H_2O} N_2 + OH + OH^- \qquad (8)$$

$$e^-(aq) + CH_2CHCONH_2 \longrightarrow \text{products} \qquad (9)$$

acrylamide complex formed for a given dose was measured for different acrylamide concentrations. For equilibrium (7) the formation constant K_7 may be expressed by (10) where $x = [Cu^IL]$ (L = acrylamide), $(a - x) = [Cu^+]$, and $(b - x) = [L]$; K_7 was obtained from the gradient of a

$$K_7 = \frac{x}{(a - x)\,(b - x)} \qquad (10)$$

linear plot of $x/(b - x)$ against x and is listed in Table 1.

The formation constants of the copper(I)–ethylene and –isobutene complexes were obtained by admitting gaseous olefin to the acrylamide system, described above, which had been γ-irradiated to produce a known amount of acrylamide complex. When the gaseous olefin was admitted to the system the optical density at 330 nm due to the acrylamide complex decreased, but was restored to its original value when the gaseous olefin was pumped off. Clearly equilibrium (11) is established under the experimental conditions and, assuming that the change in the concentration of free Cu^+ is negligibly small compared with

$$\text{copper(I)–acrylamide} + \text{olefin} \rightleftharpoons \text{copper(I)–olefin} + \text{acrylamide} \qquad (11)$$

the change in concentration of acrylamide complex, values of K_7 for the gaseous olefins can be calculated.[16] These are listed in Table 1 which also includes K_7 for copper(I)–allyl alcohol as determined by Keefer *et al.*[1]

The formation constants which we have measured are of the same order of magnitude as those reported for other such complexes.[1,4] The high value for the ethylene complex is probably due to lack of steric hindrance in this case.

Reaction of the Olefin Complexes with O_2.—*Copper*(I)*–allyl alcohol.* The complex was generated by γ-radiolysis of deaerated solutions containing 1.24 mol dm^{-3} methanol and various concentrations of Cu^{2+} and allyl alcohol. The methanol concentration was sufficiently high to ensure that virtually all the OH reacted as in (4). The irradiated solution was mixed with oxygenated water in the stopped-flow apparatus and the decay of the allyl alcohol complex was followed spectrophotometrically at 280 nm. The first 60—75% of the decay followed second-order kinetics, depending on the conditions, but became faster than second order in the final stages. The first half-life for the decay was inversely proportional to the concentration of the complex $[Cu^IL]$, and its dependence on other solute concentrations and pH is illustrated in Figure 3. The decay kinetics are described by the empirical rate law (12), and experiments at pH 1.9 confirmed that this rate law also applies in acid solution. The values of the constants k and

$$\frac{-d[Cu^IL]}{dt} = \frac{k(A + [H^+])[O_2][Cu^IL]^2}{[Cu^{2+}][L]} \qquad (12)$$

A in equation (12) are given in Table 2. No dependence of the decay rate on ionic strength (0.004—0.104 mol dm^{-3}) or methanol concentration (0.124—1.24 mol dm^{-3}) was detected.

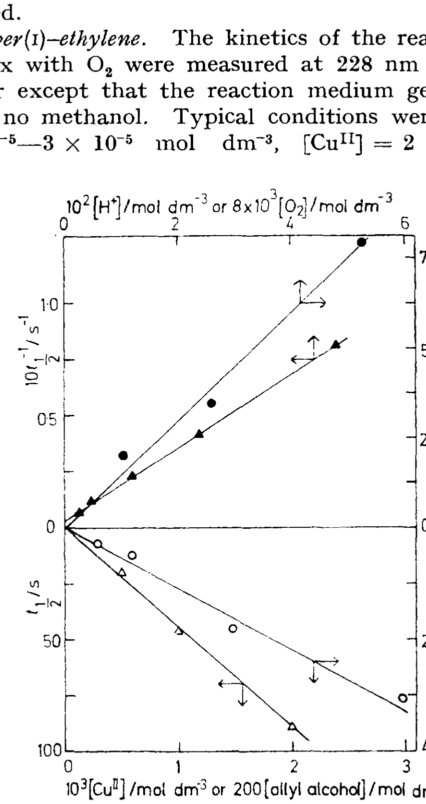

FIGURE 3 Dependence of the first half-life of the reaction of the allyl alcohol complex $[Cu^IL]$ with oxygen on: (●) O_2 ($[Cu^IL]_0 = 1.05 \times 10^{-5}$ mol dm^{-3}, $[L] = 1.47 \times 10^{-2}$ mol dm^{-3}, $[Cu^{II}] = 10^{-3}$ mol dm^{-3}, pH 4.5); (▲) pH ($[Cu^IL]_0 = 3.1 \times 10^{-5}$ mol dm^{-3}, $[L] = 0.147$ mol dm^{-3}, $[Cu^{II}] = 10^{-3}$ mol dm^{-3}, $[O_2] = 6.5 \times 10^{-4}$ mol dm^{-3}); (○) allyl alcohol ($[Cu^IL]_0 = 4.2 \times 10^{-5}$ mol dm^{-3}, $[O_2] = 6.5 \times 10^{-4}$ mol dm^{-3}, $[Cu^{II}] = 10^{-3}$ mol dm^{-3}, pH 4.5); and (△) Cu^{II} ($[Cu^IL]_0 = 4.2 \times 10^{-5}$ mol dm^{-3}, $[L] = 2.94 \times 10^{-3}$ mol dm^{-3}, $[O_2] = 6.5 \times 10^{-4}$ mol dm^{-3}, pH 4.5)

TABLE 2

Values of the constants k, A, and B in equations (12) and (13)

Eqn.	Olefin	k/dm^3 mol^{-1} s^{-1}	10^4A/mol dm^{-3}	B/dm^3 mol^{-1}
(12)	Allyl alcohol	$(1.2 \pm 0.2) \times 10^4$	1.2 ± 0.3	0
(13)	Ethylene	$(4.5 \pm 0.5) \times 10^2$	1.2 ± 0.1	115 ± 10

Copper(I)*–ethylene.* The kinetics of the reaction of the complex with O_2 were measured at 228 nm in a similar manner except that the reaction medium generally contained no methanol. Typical conditions were $[Cu^IL]_0 = 1 \times 10^{-5}$—$3 \times 10^{-5}$ mol dm^{-3}, $[Cu^{II}] = 2 \times 10^{-5}$—$2 \times 10^{-4}$ mol dm^{-3}, $[O_2] = 1 \times 10^{-4}$—7×10^{-4} mol dm^{-3}, $[C_2H_4] = 5 \times 10^{-4}$—$2.5 \times 10^{-3}$ mol dm^{-3}, and $[H^+] = 1 \times 10^{-4}$—4×10^{-3} mol dm^{-3}. The kinetics were second order for more than 2 half-lives, and the first half-life was inversely proportional to $[Cu^IL]$. For this complex, however, the rate law obtained was (13). This differs from

$$\frac{-d[Cu^IL]}{dt} = \frac{k(A + [H^+])[O_2][Cu^IL]^2}{[Cu^{2+}]} \cdot \left(B + \frac{1}{[C_2H_4]}\right) \qquad (13)$$

equation (12) in that it contains the ethylene-independent term B. This term arises because a plot of observed rate constant against $[L]^{-1}$ showed a small positive intercept on

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[16] J. C. Green, Ph.D. Thesis, University of Leeds, 1975.

the ordinate (see Figure 4). No intercepts were apparent in such plots for $[O_2]$ and $[Cu^{2+}]^{-1}$. The intercept was eliminated by the presence of 5×10^{-2} dm^{-3} methanol, making equation (13) identical in form with (12) in this case (see Figure 4). The values of the constants in equations (12) and (13) are listed in Table 2.

Hydrogen peroxide was a product of the reaction of the olefin complex with O_2 for both olefins, but only 60—70% of the theoretical yield was obtained in terms of equation (14), suggesting that some Cu^I is oxidised by the product H_2O_2. 2,3-Epoxypropan-1-ol was detected in the copper(I)–allyl alcohol + O_2 system but no ethylene oxide was detected in the corresponding ethylene system.

$$2\,Cu^I + O_2 \longrightarrow 2\,Cu^{II} + H_2O_2 \qquad (14)$$

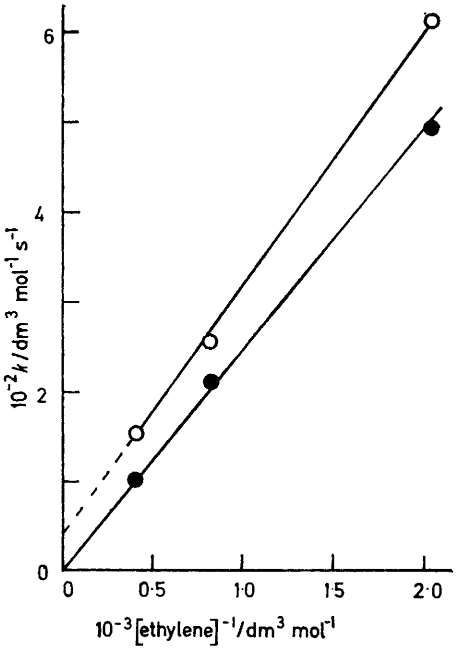

FIGURE 4 Dependence of the rate of reaction of the copper(I)–ethylene complex $[Cu^IL]$ with oxygen on $[L]^{-1}$ in the absence (○) and presence (●) of 0.05 mol dm^{-3} methanol ($[Cu^IL]_0 = 2 \times 10^{-5}$ mol dm^{-3}, $[Cu^{II}] = 10^{-4}$ mol dm^{-3}, $[O_2] = 6 \times 10^{-4}$ mol dm^{-3}, pH 4.5)

Reaction of the Olefin Complexes with H_2O_2.—The reaction of the allyl alcohol complex with H_2O_2 was examined by the method used for the oxygen reaction, except that the solutions did not contain methanol. The kinetics were not studied in detail, but they were consistent with the rate law (15) for *ca.* 75% of the reaction. No dependence on pH was observed in this case. Typical conditions were

$$\frac{-d[Cu^IL]}{dt} = \frac{k[H_2O_2][Cu^IL]^2}{[Cu^{2+}][L]} \qquad (15)$$

$[Cu^IL]_0 = 4 \times 10^{-5}$ mol dm^{-3}, $[Cu^{II}] = 10^{-3}$ mol dm^{-3}, $[L] = 7 \times 10^{-2}$ mol dm^{-3}, $[H_2O_2] = 1.3 \times 10^{-3}$ mol dm^{-3}, and $[H^+] = 10^{-2}$ mol dm^{-3} giving $k = 0.6 \pm 0.1$ s^{-1}. Rate law (15) was deduced from the effect of doubling each [solute] in turn. 2,3-Epoxypropan-1-ol was also produced by this reaction.

TABLE 3

Stoicheiometry of the reaction of the copper(I)–ethylene complex with H_2O_2 in aqueous solution at pH 3 containing 4.2×10^{-3} mol dm^{-3} C_2H_4 and 3.5×10^{-3} mol dm^{-3} H_2O_2

System [a]		Reactants consumed [a]		Product formed [a]	Stoicheiometry [b]			
					$[Cu^IL]$		C_2H_4O	
[MeOH]	$[Cu^{II}]$	$10^3[Cu^IL]$ [c]	$10^3[H_2O_2]$	$10^3[C_2H_4O]$	expt.	calc. [d]	expt.	calc. [d]
1.0	0.01	0.72	3.51	0	0.21	0.008	0	0.014
0.04	0.01	1.15	1.89	0.33	0.61	0.36	0.18	0.24
	0.01	0.75	1.11	0.32	0.68	0.52	0.29	0.74
	0.01	0.13	0.36	0.30	0.36	0.35	0.83	0.83
	0.10	0.75	1.07	0.40	0.70	1.36	0.37	0.32

[a] Concentrations in mol dm^{-3}. [b] Based on H_2O_2 = 1. [c] All the ethylene complex was consumed. [d] From equation (32) (see Discussion).

The kinetics of the reaction of the ethylene complex with H_2O_2 were not investigated, but the stoicheiometric relation between reactants and products was examined in some detail. The relevant data are summarised in Table 3. After generation of the ethylene complex by radiolysis of the particular system (see Table 3), 10^{-5} dm^3 of '40-volume' H_2O_2 was injected into the irradiated solution through a serum cap. The solutions were analysed for H_2O_2 and ethylene oxide when all the complex had reacted. The data in Table 3 clearly indicate that decomposition of H_2O_2 occurs in a chain reaction.

DISCUSSION

Mechanism of the $[Cu^IL] + O_2$ *Reaction*.—The following mechanism is proposed for the oxidation of the copper(I)–olefin complexes by O_2:

$$Cu^I + L \rightleftharpoons [Cu^IL] \qquad (7)$$

$$Cu^I + O_2 \rightleftharpoons [Cu^IO_2] \qquad (16)$$

$$[Cu^IO_2] + H^+ \rightleftharpoons [Cu^{II}(O_2H)] \qquad (17)$$

$$[Cu^{II}(O_2H)] \rightleftharpoons Cu^{II} + HO_2 \qquad (18)$$

$$HO_2 \rightleftharpoons H^+ + O_2^- \qquad (19)$$

$$O_2^- + Cu^{II} \rightleftharpoons [Cu^IO_2] \qquad (20)$$

$$HO_2 + [Cu^IL] \xrightarrow{H^+} Cu^{II} + L + H_2O_2 \qquad (21)$$

$$O_2^- + [Cu^IL] \xrightarrow{2H^+} Cu^{II} + L + H_2O_2 \qquad (22)$$

If all the equilibria are rapidly established this mechanism leads to the rate law (23), which has the same form as (12) and (13) when $B = 0$ in the latter case. An

$$\frac{-d[Cu^IL]}{dt} = \frac{k_{21}K_{16}K_{17}K_{18}}{K_7}\left(\frac{K_{19}k_{22}}{k_{21}} + [H^+]\right)\frac{[O_2][Cu^IL]^2}{[Cu^{II}][L]} \qquad (23)$$

alternative mechanism is reaction (7) followed by (24), (19), (21), and (22), in which case the rate law would be (25). This rate law also has the required form, but the

$$\mathrm{Cu^I} + \mathrm{O_2} \rightleftharpoons \mathrm{Cu^{II}} + \mathrm{O_2^-} \qquad (24)$$

$$\frac{-\mathrm{d[Cu^IL]}}{\mathrm{d}t} = \frac{k_{22}K_{24}}{K_7}\left(1 + \frac{k_{21}[\mathrm{H^+}]}{k_{22}K_{19}}\right)\frac{[\mathrm{O_2}][\mathrm{Cu^IL}]^2}{[\mathrm{Cu^{II}}][\mathrm{L}]} \qquad (25)$$

mechanism from which it is derived can be ruled out for the following reason. The standard redox potential of Cu^+–Cu^{2+} is $+0.15$ V [17] and that of O_2–O_2^- is -0.325 V [18] so that $K_{24} \sim 10^{-8}$. For allyl alcohol $K_7 = 5.2 \times 10^4$ dm^3 mol^{-1} (Table 1), and therefore k_{22} would have to be absurdly large to account for the observed rate constant (kA in Table 2) of the decay of the allyl alcohol complex of *ca.* 1.8 s^{-1} at pH 4.5.

Meisel *et al.*[19] obtained evidence which supports the existence of the species $[Cu^{II}(O_2H)]$ in equilibrium (18) and they estimated $K_{18} = 2 \times 10^{-8}$ mol dm^{-3}. They also pointed out [19] that $[Cu^{II}(O_2H)]$ might resemble the $[Cu^IO_2]$ complex in reaction (16) which has been suggested as an intermediate in a number of other $Cu^I + O_2$ systems.[5,7-9] Despite the low value of K_{18}, HO_2 and O_2^- must be invoked as the oxidants of $[Cu^IL]$ in order to account for the inverse dependence on $[Cu^{II}]$ and the observed pH dependence [equations (12) and (13)].

The data in Table 2 show that A has the same value in equations (12) and (13). If equation (23) is correct, $A = K_{19}k_{22}/k_{21}$ and since $K_{19} = 1.25 \times 10^{-5}$ mol dm^{-3},[20] $k_{22}/k_{21} = 9.2$ for both olefin complexes. This value is similar to that reported [21] for the reaction of O_2^- and HO_2 with Cu^+. If equation (23) is correct the parameter k in (12) and (13) is identified with $k_{21}K_{16}K_{17}K_{18}/K_7$. Taking K_7 from Table 1, and noting that K_{16}, K_{17}, and K_{18} are independent of olefin, we find that k_{21} and k_{22} for the allyl alcohol system are six times larger than for the ethylene system.

A lower limit for the quantity $K_{16}K_{17}$ can be estimated since k_{22} for the allyl alcohol complex cannot exceed *ca.* 10^{10} dm^3 mol^{-1} s^{-1}, and hence $k_{21} \leqslant \sim 10^9$ dm^3 mol^{-1} s^{-1}. Combining this value with K_{18} given above and the value of k for the allyl alcohol complex in Table 2 we obtain $K_{16}K_{17} \geqslant 10^5$ dm^6 mol^{-2}, which is not an unreasonable value.

It is significant that the parameter B in equation (13) was zero when 5×10^{-2} mol dm^{-3} methanol was present (see Figure 3). Under these conditions reaction (4) will compete effectively with reaction (26), and this suggests

$$\mathrm{OH} + \mathrm{C_2H_4} \longrightarrow \cdot\mathrm{CH_2CH_2OH} \qquad (26)$$

that the appearance of B in the rate law (12) may be due to a reaction of $\cdot CH_2CH_2OH$. Since H_2O_2 is a product, reaction (6) will be a source of OH. The occurrence of reaction (27), for which $k_{27} = 7.8 \times 10^7$ dm^3 mol^{-1} s^{-1},[22] is the most likely cause for $B \neq 0$ in the absence of methanol. Competition between reactions (6) and (16), and between reactions (27) and (28) (see below), could account for the lack of an intercept in the plots of first half-life for the decay of the ethylene complex against $[O_2]$ and $[Cu^{II}]$ respectively.

$$\cdot\mathrm{CH_2CH_2OH} + [\mathrm{Cu^IL}] \longrightarrow \mathrm{Cu^{II}} + \text{products} \qquad (27)$$

Comparison with other Work.—Table 4 summarises the rate-law data for the reaction of various copper(I) complexes with O_2 obtained by a number of other workers and ourselves, and two major differences are evident. Thus, in most other studies the observed rate law is first order in $[Cu^IL]$, and apparently zero order in $[Cu^{II}]$. These observations can be explained if the forward reaction of equilibrium (18) is rate determining, which could be expected at sufficiently high $[Cu^IL]$ and low $[Cu^{II}]$ where reactions (21) and (22) become rapid compared to the rate at which equilibrium (18) is established.

TABLE 4

Concentration dependences of the rate of reaction of copper(I) complexes with O_2

Ligand L	Order of dependence on:					Ref.
	$[O_2]$	$[Cu^IL_n]$	[L]	$[H^+]$	$[Cu^{II}]$	
Cl^-	1			1		5
Cl^-	1	2				6
Imidazole or NH_3	1	1	1			7
2,2′-Bipyridine	1	1				8
Acetonitrile	1	1	−2	1		9
Acetonitrile	1	1	−2 and −3	0 and 1		10
Histamine	1	1				*a*
Dimethyl sulphoxide	1	1		0 and 1		11
Allyl alcohol	1	2	−1	0 and 1	−1	*b*
Ethylene	1	2	0 and −1	0 and 1	−1	*b*

[a] A. Zuberbühler, *Helv. Chim. Acta*, 1970, **53**, 669. [b] This work.

Mechanism of the $[Cu^IL] + H_2O_2$ *Reaction.*—A mechanism which is consistent with our experimental observations is reaction (6) and (7) followed by (26), (28), and (27). Applying the steady-state approximation to

$$\mathrm{OH} + \text{olefin} \longrightarrow \mathrm{R} \qquad (26)$$

$$\mathrm{R} + \mathrm{Cu^{II}} \longrightarrow \mathrm{Cu^I} + \text{epoxide} \qquad (28)$$

$$\mathrm{R} + [\mathrm{Cu^IL}] \longrightarrow \mathrm{Cu^{II}} + 2\ \mathrm{L} \qquad (27)$$

the radicals R and OH we obtain equation (29). This is

$$\frac{-\mathrm{d[Cu^IL]}}{\mathrm{d}t} = \frac{k_6k_{27}[\mathrm{H_2O_2}][\mathrm{Cu^IL}]^2}{K_7[\mathrm{L}](k_{27}[\mathrm{Cu^IL}] + k_{28}[\mathrm{Cu^{II}}])} \qquad (29)$$

of the same form as the observed rate law (15) if $k_{28}[Cu^{II}] \gg k_{27}[Cu^IL]$. The inverse dependence on [L] indicates that $[Cu^IL]$ does not react with H_2O_2 at a significant rate. This mechanism constitutes a chain reaction propagated by reactions (6), (26), and (28), and terminated by (27).

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When reaction (27) does not occur the catalytic decomposition of H_2O_2 should go to completion. Table 3 shows this to be the case for the system containing 1 mol dm^{-3} methanol when virtually all OH react as in (4). Evidently $\cdot CH_2OH$ does not react at a significant rate with the ethylene complex, and this is in accord with our observation that $B = 0$ in equation (13) in the oxygen system containing methanol (see Figure 4) when reaction (27) is unimportant.

The decrease in the number of H_2O_2 decomposed per ethylene complex when [MeOH] was decreased (see Table 3) can be accounted for qualitatively in terms of the increasing competition between reactions (26) and (4), making (27) more probable. Similarly, the increased catalytic decomposition of H_2O_2 as $[Cu^IL]$ (L = ethylene) was lowered is the expected result because reaction (28) competes more favourably with (27). On the other hand an increase in $[Cu^{II}]$ would also be expected to increase the decomposition of H_2O_2 for the same reason, but this was not observed. In order to account for this we suggest that reactions (30) and (31) provide an additional termination mechanism which counterbalances the increased probability of reaction (28). The value of

$$OH + Cu^{II} \longrightarrow Cu^{III} \qquad (30)$$

$$Cu^{III} + [Cu^{I}L] \longrightarrow 2\,Cu^{II} + L \qquad (31)$$

k_{30} is 3.5×10^8 dm^3 mol^{-1} s^{-1},[23] and k_{26} for ethylene is 4.1×10^9 dm^3 mol^{-1} s^{-1},[24] so that 15% of OH will be chain terminators when $[Cu^{II}] = 10^{-2}$ mol dm^{-3} and 63% when $[Cu^{II}] = 10^{-1}$ mol dm^{-3}. Copper (III) is unreactive towards methanol[25] so it is unlikely to react with ethylene. For the allyl alcohol system the quotient $[L]/[Cu^{II}]$ was $\geqslant 35$ so that reaction (30) was unimportant in this case.

When reactions (4), (30), and (31) are included in the mechanism for the reaction of the ethylene complex with H_2O_2 the predicted stoicheiometry is given by (32) where f_4 and f_{26} are the fractions of the total OH which react

$$H_2O_2 + 2(1 - f_{26}f_{28} - f_4)[Cu^IL] \longrightarrow f_{26}f_{28}C_2H_4O \qquad (32)$$

with methanol and ethylene respectively and f_{28} is the fraction of the total $\cdot CH_2CH_2OH$ which react with Cu^{II}. Using values of k_{26}, k_{27}, and k_{30} given above, $k_4 = 8 \times 10^8$ dm^3 mol^{-1} s^{-1},[26] and $k_{28} = 2 \times 10^7$ dm^3 mol^{-1} s^{-1},[22] to calculate f_4, f_{26}, and f_{28}, we obtain from equation (32) the calculated stoicheiometries shown in Table 3, where they are compared with the experimental values. Because termination by reaction (27) decreases as the ethylene complex is consumed, the calculated stoicheiometries were obtained by numerical integration. Although the calculated and experimental stoicheiometries do not all agree very well, their similar trends are in accord with the proposed mechanism. It is clear from equation (32) that the most efficient catalytic oxidation of ethylene will occur when $f_{26}f_{28}$ approaches unity. Such a condition requires $k_{26}[C_2H_4] \gg k_{30}[Cu^{II}]$ and $k_{28}[Cu^{II}] \gg k_{27}[Cu^IL]$.

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