Reaction of the Aquacopper(I) Ion with Hydrogen Peroxide

Evidence for a Cu^{III} (Cupryl) Intermediate

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> Oxidation of CH₃OH to HCHO occurs as a chain reaction on γ -irradiation of deaerated aqueous CH₃OH + H₂O₂ + Cu²⁺_{aq} solutions. The reaction of Cu⁺_{aq} with H₂O₂ is a propagation step. The chain-length and the dependence of HCHO formation rate on radiation dose, CH₃OH concentration and pH are not compatible with a mechanism that includes production of the free hydroxyl radical, OH⁺, by the Cu⁺_{aq} + H₂O₂ reaction. It is suggested that an intermediate is formed by this reaction that reacts with methanol with a rate constant not greater than 4×10^5 dm³ mol⁻¹ s⁻¹, and the main features of the results are explained on this basis. The reactivity of the proposed intermediate is shown to be similar to that of the Cu^{III}_{aq} (cupryl) species, produced by reaction of OH⁺ with Cu²⁺_{aq}.

The reaction of H_2O_2 with Cu¹ ions in biological systems can lead to cell damage and the reactive intermediate responsible has usually been assumed to be the hydroxyl free radical (OH[•]), although other possibilities have been considered.¹ Most Cu^I complexes react rapidly with H_2O_2 , but studies of the Cu^I + H_2O_2 reaction have been made mainly in systems where the metal is complexed by ligands, such as 1,10-phenanthroline²⁻⁵ and 2,2'-bipyridyl,^{6,7} that form stable complexes with Cu^I. From the point of view of understanding the role of Cu^I in biological oxidation, information is also needed about the reactions of H_2O_2 with less stable Cu^1 complexes and with the aquacopper(1) ion (Cu_{aq}^{+}) . In these cases, the possibility of disproportionation of Cu^{I} to Cu^{II} and Cu^{0} severely restricts the concentration range of Cu^I that can be used.⁸ We report here an investigation in which γ -irradiation of aqueous solutions of Cu²⁺_{aq} and CH₃OH was used to produce Cu_{aa}^{+} , at a known rate, to study its reaction with H_2O_2 . Under the conditions used, the stationary concentration of Cu⁺_{aq} is sufficiently low to preclude disproportionation. The investigation, a preliminary account of which has been published,⁹ was aimed primarily at determining whether or not OH[•] is formed by reaction of H_2O_2 with Cu_{aq}^+ .

Experimental

Materials were A.R. grade, and were used as received. Solutions were in triply distilled water. pH was adjusted by addition of H_2SO_4 . Stock H_2O_2 solutions, prepared from unstabilised H_2O_2 (Laporte) were standardised spectrophotometrically using iodide reagent.¹⁰

The solutions for irradiation were mixed in a Pyrex glass vessel, fitted with a rubber septum cap, and were saturated with either N_2O or N_2 by bubbling. *y*-Irradiations (⁶⁰Co source, nominally 800 Ci) were at constant dose rate, determined by Fricke dosimetry.

In experiments with H_2O_2 present, under certain conditions there was significant formation of HCHO in the unirradiated solution, presumably due to the thermal reaction of H_2O_2 with CH₃OH, catalysed by copper ions. This 'dark reaction' was negligible at pH < 3, but increased in rate with increasing pH. To minimise its

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contribution to the total yield, H_2O_2 was introduced immediately before irradiation, and the solution was acidified to pH < 3 immediately after irradiation. For each radiation yield measurement, unirradiated controls were analysed, together with the irradiated solutions. The results have been corrected for the contribution of the dark reaction, which was never greater than *ca.* 10% of the radiation yield. Samples were taken immediately after irradiation for analysis, together with the appropriate controls.

HCHO was measured by the 2,4-dinitrophenylhydrazone method.¹¹ Cu_{aq}^+ was determined as its complex with 2,9-dimethyl-1,10-phenanthroline.¹¹

Results

Radiation-induced Reactions

The γ -ray-induced decomposition of water, which forms free-radical species, via reaction (1)

$$H_2O \longrightarrow OH', H', e_{aq}^-, H_2O_2, H_2$$
 (1)

was used to generate Cu_{aq}^+ at a steady rate from a solution containing CH₃OH (0.1-2.0 mol dm⁻³), and copper(II) sulphate [(1-20) × 10⁻³ mol dm⁻³], saturated with N₂O (*ca.* 3 × 10⁻² mol dm⁻³). The main reactions in this system,¹² together with reported rate constant values, are collected in table 1.

Under the conditions used, each radiation-produced free radical reacts to give Cu_{aq}^+ , either directly or indirectly, and the rate of Cu_{aq}^+ production, via the radical reactions, is given by $R(Cu_{aq}^+) = G_i D$, where $G_i = G(OH^+) + G(e_{aq}^-) + G(H^+)$ is the total radiation yield of free radicals and D is the dose rate. $G(H^+) = 0.054 \ \mu \text{mol J}^{-1}$ was assumed, and the total radiation yield of OH⁺ from N₂O-saturated solution, which depends on CH₃OH concentration, was calculated from the expression:¹⁸

$$G(OH^{-})/\mu mol J^{-1} = 0.54 + 0.31 (k_5 [CH_3OH]/\lambda)^{\frac{1}{2}} / \{1 + (k_5 [CH_3OH]/\lambda)\}^{\frac{1}{2}}$$

where $\lambda = 4.7 \times 10^8 \text{ s}^{-1}$. This gives $G(\text{OH}^{-}) = 0.60-0.73 \,\mu\text{mol J}^{-1}$ over the CH₃OH concentration range 0.1-2.0 mol dm⁻³, *i.e.* $R(\text{Cu}_{aq}^+) = (5.6-6.2) \times 10^{-7} \text{ mol dm}^{-3} \text{ s}^{-1}$ for a dose rate of 0.8 Gy s⁻¹.

Yields in the Absence of H₂O₂

Irradiation of solutions of $Cu_{aq}^{2+}+CH_3OH$ (N₂O-saturated) gave HCHO and Cu_{aq}^+ yields directly proportional to the total dose (20–100 Gy): table 2 gives G(HCHO) and $G(Cu_{aq}^+)$ for [CH₃OH] = 0.025 and 0.25 mol dm⁻³.

Yield measurements were also made for solutions with Cu_{aq}^{2+} in excess over CH_3OH at pH 1.9–5.4 (table 3).

Yields in the Presence of H₂O₂

With H_2O_2 present, the yield of HCHO from $Cu_{aq}^{2+} + CH_3OH$ solutions (N₂O-saturated) was directly proportional to the total dose, with G(HCHO) significantly greater than in the absence of H_2O_2 . Fig. 1 shows the linear dependence of the HCHO yield on time, for constant dose rate (0.80 Gy s⁻¹), obtained with [CH₃OH] = 1.0 mol dm⁻³, [H₂O₂] = 3×10^{-3} mol dm⁻³, [Cu_{aq}⁺] = 1.0×10^{-3} mol dm⁻³. No Cu_{aq}⁺ could be detected when H_2O_2 was present.

R(HCHO) was determined for a variety of initial conditions. In each case, the HCHO concentration was measured in samples irradiated with different total radiation doses, the maximum dose (*ca.* 80 Gy) being sufficiently low to avoid significant reagent depletion. The quoted values of R(HCHO) are means of measurements from at least three separate irradiations. Except where stated, the separate measurements agreed, within the experimental uncertainty of *ca.* 10%.

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reaction		$k/10^8 \mathrm{dm^3 mol^{-1} s^{-1}}$	ref.
$e_{aa}^- + N_aO(+H^+) \rightarrow N_a + OH^-$	(2)	80	13
$\tilde{e}_{aa}^{-} + Cu_{aa}^{2+} \rightarrow Cu_{aa}^{+}$	(3)	300	13
$e_{aa}^{a} + H^{a} \rightarrow H^{aa}$	(4)	200	13
$OH' + CH, OH \rightarrow CH, OH + H, O$	(5)	8.0	14
H [•] +CH ₃ OH → [•] CH ₃ OH + H ₃	(6)	0.02	15
$H' + Cu_{2a}^{2+} \rightarrow Cu_{aa}^{+} + H^{+}$	(7)	0.7	16
$CH_{2}OH + Cu_{aq}^{aq} \rightarrow HCHO + Cu_{aq}^{+} + H^{+}$	(8)	1.6	17

Table 1. Reactions in γ -irradiated Cu²⁺_{aq} + CH₃OH solutions

Table 2. Formation of HCHO and Cu_{aq}^+ in γ -irradiated solutions of $CH_3OH + Cu_{aq}^{2+}$ (N₂O-saturated, pH 3.0)^a

$[CH_{3}OH]/10^{-2} \text{ mol } dm^{-3}$	G	(HCH	D)		$G(\mathrm{Cu}_{\mathrm{aq}}^+$)	
2.50	<i>b</i> 0.62	<i>c</i> 0.58	d 0.65	<i>b</i> 0.55	<i>c</i> 0.50	<i>d</i> 0.64	
25.0	0.68	0.68	0.76	0.61	0.57	0.71	

^{*a*} Measured and calculated radiation yields [$G(\text{product}/\mu\text{mol } J^{-1})$] in the absence of H_2O_2 . [$Cu_{aq}^{2+1} = 1 \times 10^{-3} \text{ mol } dm^{-3}$, dose rate = 0.8 Gy s⁻¹. Standard deviation on measured values < 0.2 for four independent measurements (total dose = 20–100 Gy). ^{*b*} Measured values. ^{*c*} Calculated values assuming radiation-produced H_2O_2 does not give OH⁺. ^{*d*} Calculated values assuming radiation-produced H₂O₂ gives OH⁺ (see Discussion).

Table 3. Formation of HCHO and Cu_{aq}^+ in γ -irradiated solutions of CH₃OH (5 × 10⁻⁴ mol dm⁻³, Cu_{aq}^{2+} (0.01 mol dm⁻³), N₂O-saturated^a

pН	1.9	3.0	3.5	4.8	5.4
G(HCHO) $G(\text{Cu}_{aq}^+)$	0.41 (0.06) 0.63 (0.06)	0.43 (0.05)	0.27 (0.07)	0.10 (0.02)	0.10 (0.07)

^{*a*} Dependence of $[G(\text{product})/\mu \text{mol } J^{-1}]$ on pH. Dose rate = 0.8 Gy s⁻¹. Standard deviation (in parentheses) from 4 independent measurements for total radiation dose 20–100 Gy.

R(HCHO) was independent of whether N₂O or N₂ was used as the deaerating gas. Solutions saturated with N₂O containing 0.1 atm O₂ (solution $[O_2] \approx 10^{-4} \text{ mol dm}^{-3}$) instead of pure N₂O gave the same value of R(HCHO) as in the absence of H₂O₂. At constant H₂O₂ and CH₃OH concentrations, R(HCHO) increased with decreasing pH (table 4).

Fig. 2 shows the dependence of R(HCHO) on CH_3OH concentration for $[H_2O_2] = 3.0 \times 10^{-3}$ mol dm⁻³ at pH 3.0 and 5.0. Values of R(HCHO) obtained with various initial concentrations of H_2O_2 , Cu_{aq}^{2+} , and dose rates are collected in table 5 (pH 5.2) and table 6 (pH 3.0).

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Fig. 1. Formation of HCHO from solutions of CH₃OH (1.0 mol dm⁻³), H₂O₂ (3×10^{-3} mol dm⁻³), Cu²⁺_{aq} (1×10^{-3} mol dm⁻³), N₂O-saturated (pH 5.2) γ -irradiated at constant dose-rate (*ca.* 0.8 Gy s⁻¹). Dependence of HCHO yield on time. \bigcirc , Measured values. Lines show values calculated using FACSIMILE: (····) OH '-radical mechanism, (----) proposed mechanism (see text).

Table 4. Formation of HCHO in γ -irradiated solutions CH₃OH (1.0 mol dm⁻³), Cu²⁺_{3q} (0.001) mol dm⁻³), H₂O₂ (0.003 mol dm⁻³), N₂O-saturated: dependence of rate of HCHO formation, *R*(HCHO), on pH^a

CHO)/10 ⁻⁶ mol dm ³ s ⁻¹
6.4 (0.3)
8.8 (0.8)
15.8 (0.7)
15.4 (1.0)
15.4 (1.6)
18.8 (1.4)
27.4 (1.3)
83 ^b
108°

^{*a*} Dose rate = 0.8 Gy s^{-1} . Standard deviation (in parentheses) from 3 independent measurements for total radiation dose 20–40 Gy. ^{*b*} Values based on measurement for dose = 20 Gy.

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Fig. 2. Formation of HCHO from solutions of CH₃OH (1.0 mol dm⁻³), H₂O₂ (3×10^{-3} mol dm⁻³), Cu⁺²_{aq} (1×10^{-3} mol dm⁻³) N₂O-saturated (pH 5.2) γ -irradiated at constant dose rate (*ca*. 0.8 Gy s⁻¹). Dependence of rate of HCHO formation, *R*(HCHO), on CH₃OH concentration at pH 3.0 (\bigoplus) and pH 5.2 (\bigcirc). Calculated values (\times) (see text).

Table 5.	Formation	of HCHO	from	γ-irradiated	solutions	of	$CH_3OH + H_2O_2 +$	$+Cu_{aq}^{2+}$	$(N_2O-$
saturated	, pH 5.2): de	pendence o	f rate	of HCHO for	mation, R((HC	(HO), on initial co	oncentr	ations
		-	;	and initiation	rate ^a				

	[H ₂ O ₂] /10 ⁻³ mol dm ⁻³			R(HCHO) /10 ⁻⁷ mol dm ⁻³ s ⁻¹		
[Cu ²⁺] 10 ⁻³ mol dm ⁻³		[CH ₃ OH] /mol dm ⁻³	$R_{\rm i}$ - /10 ⁻⁷ mol dm ⁻³ s ⁻¹	obs.	calc.	
1.0	3.0	1.0	5.0	8.8	9.2	
1.0	0.68	0.5	5.0	4.9	3.6	
1.0	1.2	1.0	5.0	6.3	6.4	
1.0	1.2	0.5	5.0	5.6	4.7	
1.0	1.4	0.05	5.0	1.8	1.7	
1.0	3.0	0.05	5.0	1.6	1.7	
1.0	3.4	0.25	5.0	4.1	4.3	
1.0	0.88	0.10	5.0	2.3	2.1	
2.0	0.88	0.10	5.0	2.3	2.1	
2.5	1.3	0.5	5.0	5.6	4.8	
10.0	3.0	1.0	5.0	9.0	9.2	
1.0	1.0	0.1	5.5	2.2	2.0	
1.0	1.0	0.1	0.72	4.5	4.0	
1.0	3.4	1.0	0.56	13	19	
1.0	3.4	1.0	5.0	8.2	9.5	

^a Calculated rates from FACSIMILE (see Discussion).

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[H2O2] /10 ⁻³ mol dm ⁻³	[CH ₃ OH] /10 ⁻³ mol dm ⁻³	R(HCHO) /10 ⁻⁶ mol dm ⁻³ s ⁻¹
1.2	0.5	18
1.2	0.5	19
3.0	0.5	12
3.2	0.5	12
0.60	0.5	22
6.0	0.5	6.3
10	0.5	6.2
1.2	0.1	10
3.2	0.1	6.0

Table 6. Formation of HCHO in γ -irradiated solutions of CH₃OH+H₂O₂+Cu²⁺_{aq} (N₂O-saturated): dependence of rate of HCHO formation, *R*(HCHO), on H₂O₂ and CH₃OH concentration at pH 3.0

Discussion

The rate of HCHO formation, on irradiation at constant dose rate, was significantly increased by H_2O_2 , indicating that HCHO is formed by a chain reaction under these conditions. It is assumed that this chain reaction is initiated by the radiation-induced production of Cu_{aq}^+ and that the chain process includes reaction of Cu_{aq}^+ with H_2O_2 as a propagation step. This is consistent with the observed inhibition of the chain reaction by relatively low concentrations of O_2 because the fast reaction of Cu_{aq}^+ with O_2 can prevent its reaction with H_2O_2 .

The initiating reactions (1)-(8) are not influenced by the presence of low concentrations of H_2O_2 , and the net effect of γ -irradiation is to introduce Cu_{aq}^+ into the system at a known rate, *i.e.* rate of initiation $R_i = R(Cu_{aq}^+) = G(Cu_{aq}^+) D$.

If OH is formed in the $Cu_{ao}^+ + H_2O_2 + CH_3OH$ system by the reaction

$$Cu_{aq}^{+} + H_2O_2 \rightarrow Cu_{aq}^{2+} + OH^{-} + OH^{-}$$
(9)

chain oxidation of CH_3OH to HCHO would be expected, with reactions (5), (8) and (9) as propagation steps. At sufficiently high CH_3OH concentration, reactions of OH' with species present at relatively low concentrations (including H_2O_2 , copper ions, intermediates and products) cannot compete successfully with reaction (5) and can, therefore, be excluded as termination steps. Termination by reaction of 'CH₂OH with Cu_{aq}^+ can also be excluded, since there is strong evidence that oxidation of Cu_{aq}^+ by 1-hydroxyalkyl radicals does not occur.¹⁷ This leaves the radical-combination reaction (10)

$$2^{\circ}CH_{2}OH \rightarrow products$$
 (10)

 $[k_{10} = 1 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}, \text{ ref. (19)}]$ as the most probable chain-termination step.

The kinetic behaviour resulting from a mechanism consisting of steady formation of Cu_{aq}^{+} , and reactions (5), (8), (9) and (10) can be predicted. For this purpose we assumed that $k_9 = 4 \times 10^3$ dm³ mol⁻¹ s⁻¹, the value determined by direct measurement of the rate of reaction of Cu_{aq}^{+} with H_2O_2 .²⁰ This is close to the value^{3,5} (2 × 10³ dm³ mol⁻¹ s⁻¹) of the rate constant for the analogous reaction of the bis(1,10-phenanthroline)copper(I) ion with H_2O_2 . It is apparent that reaction (9) is rate-limiting, and Cu_{aq}^{+} does not attain a steady state with this mechanism. For comparison with the experimental results, therefore, the kinetics were modelled by numerical integration using the FACSIMILE program.²¹ Fig. 1 shows the calculated dependence of HCHO yield on time, together

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with the experimental values. Obviously, this mechanism is not consistent with the observed constant rate of HCHO formation, and predicts a rate of CH_3OH oxidation much faster than observed. As well as these differences, other features of the reaction differ from those expected on the basis of the mechanism involving OH⁺ radical formation by reaction (9). The HCHO yield (fig. 1) calculated from this mechanism is independent of the CH₃OH concentration, whereas the measured *R*(HCHO) was dependent on the CH₃OH concentration (fig. 2). Furthermore, there are no obviously pH-dependent steps in the OH⁺ mechanism, whereas the measured *R*(HCHO) was dependent on pH (table 4).

The main features of our results can be explained if it is assumed that the intermediate, formed by reaction of Cu_{aq}^+ with H_2O_2 , is not OH⁺, but a species with a rate constant for its reaction with CH_3OH much smaller than that of OH⁺. Reaction of the intermediate with Cu_{aq}^+ can then be a significant termination reaction. This is represented schematically by reactions (11)–(13), where Cu^{III} is the postulated intermediate.

$$Cu_{aa}^{+} + H_2O_2 \rightarrow Cu^{III}$$
(11)

$$Cu^{III} + CH_3OH \rightarrow CH_2OH + Cu^{2+}_{aa} + H^+$$
(12)

$$Cu^{III} + Cu^{+}_{aq} \rightarrow 2Cu^{2+}_{aq}.$$
 (13)

For a mechanism with initiation by the radiation-induced formation of Cu_{aq}^+ , propagation by reactions (11), (12), and (8), and termination by reaction (13), assuming Cu_{aq}^+ , CH_2OH and Cu^{III} to be in the steady state, the rate is given by

$$R(\text{HCHO}) = R_{i} + (R_{i}k_{11}k_{12}[\text{CH}_{3}\text{OH}][\text{H}_{2}\text{O}_{2}]/2k_{13})^{\frac{1}{2}}.$$
 (14)

At pH 5.2, with constant $[H_2O_2]$, the observed R(HCHO) increased linearly with $[\text{CH}_3\text{OH}]^{\frac{1}{2}}$, as predicted from eqn (14), at least over the range 0.25–2.0 mol dm⁻³ (fig. 2). Assuming the concentration dependence in this concentration range to be described by eqn (14), from the slope of the linear section of the plot, a value is obtained for the rate constant ratio $k_0 = k_{11}k_{12}/k_{13} = 0.14 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. At low CH₃OH concentration (< 0.25 mol dm⁻³), the measured values of R(HCHO)

At low CH₃OH concentration (< 0.25 mol dm⁻³), the measured values of R(HCHO) were somewhat lower than predicted from eqn (14). This is apparent in fig. 2, where the lines, obtained from the data by linear regression, show small negative intercepts at $[CH_3OH]^{\frac{1}{2}} = 0$. A suggested explanation is that a termination reaction

$$Cu^{III} + H_2O_2 \rightarrow products$$
 (15)

occurs in competition with reactions (12) and (13). The FACSIMILE program²¹ was used to compute the dependence of R(HCHO) on CH₃OH concentration from the mechanism including reaction (15). For this purpose, the value of $k_0 = 0.14 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, was used, and the value of k_{15} varied to obtain the best fit. The calculated R(HCHO) values (fig. 2 and table 5) were obtained with $k_{15} = 2 \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.

On the basis of the above treatment, an upper limit for the value of k_{12} can be estimated. Taking $k_{11} = 4 \times 10^3$ dm³ mol⁻¹ s⁻¹, *i.e.* the same value as that assumed above for k_9 , and taking as an upper limit the value of $k_{13} = 10^{10}$ dm³ mol⁻¹ s⁻¹ (*i.e.* equal to the diffusion-controlled limit for neutral species²²), gives $k_{12} \leq 4 \times 10^5$ dm³ mol⁻¹ s⁻¹.

HCHO Formation in the Absence of Added H₂O₂

HCHO is formed in the γ -irradiated $Cu_{aq}^{2+} + CH_3OH$ system ([CH₃OH] \geq [Cu_{aq}²⁺]) via reactions (5), (6) and (8).¹⁷ Under these conditions the metastable Cu_{aq}^+ ion accumulates as a product in the irradiated solution. Since water radiolysis also gives some H₂O₂, with a radiation yield of $G(H_2O_2) = 0.073 \ \mu mol \ J^{-1}$, the total expected yields of HCHO and Cu_{aq}^+ depend on how this H₂O₂ reacts with Cu_{aq}^+ . If reaction (9) occurs, an additional radiation yield of HCHO equal to $G(H_2O_2)$ will be formed, via reactions (9), (5) and (8),

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but the Cu_{aq}^+ yield will not be affected. On the other hand, if H_2O_2 reacts via reactions (11)-(13) and $k_{12}/k_{13} = 4 \times 10^{-5}$, as deduced above, there will be essentially no contribution to the HCHO yield from the reaction of H_2O_2 , but Cu_{aq}^+ will be removed via reactions (11) and (13). The expected yields of HCHO and Cu⁺_{aq}, in either case, depend on the values assumed for the radiation yields of the radical species and, unfortunately, the uncertainties associated with these values,¹⁸ particularly at solute concentrations above 10⁻⁴ mol dm⁻³, make it difficult to use this method to distinguish between the two mechanisms. For the conditions used to obtain the measured values of G(HCHO) and $G(Cu_{aa}^{+})$, the theoretical values were calculated using the best estimated values of $G(OH^{+})$ and allowing for the competitions between reactions (2) and (3) and between reactions (6) and (7). The theoretical values are closest to the measured values (table 2) in the case of the mechanism that assumes that OH' is not formed via reaction (9). Although, because of the uncertainties associated with both the measured and theoretical values, this finding alone cannot be taken as firm evidence, it can at least be concluded that the measured G(HCHO) and $G(Cu_{aq}^{+})$, in the absence of added H₂O₂ at pH 5.2, are not inconsistent with the mechanism involving reactions (11)-(13).

Nature of the Intermediate

There have been earlier suggestions^{7, 23-26} that OH may not be formed by reaction of Cu^{I} ions with H_2O_2 , and the formation of cupryl species, with Cu in the formal +3 oxidation state, has been considered. Production of Cu_{aq}^{III} by addition of OH to Cu_{aq}^{II} .

$$OH' + Cu_{aq}^{2+} \rightarrow Cu_{aq}^{III}$$
(16)

 $(k_{16} = 3 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1})$ has been demonstrated by pulse radiolysis.²⁷⁻²⁹ The same species could possibly be formed by reaction of Cu_{aq}^+ with H_2O_2 , e.g. an initial reaction to give a copper- H_2O_2 complex, followed by electron-transfer and rearrangement within the complex. It is of interest, therefore, to compare the reactions of Cu_{aq}^{III}, produced by reaction of OH with Cu^{II}_{ao}, with those of our postulated intermediate. Reactions of the species from pulse radiolysis with various solutes, including H₂O₂ and CH₃OH, have been investigated²⁸ in the pH range 3-6. At pH 5.4, the reaction with CH₃OH was slow, compared with its other reactions under pulse radiolysis conditions, and only an upper limit was obtained for the rate constant, $k \leq 1 \times 10^6$ dm³ mol⁻¹ s⁻¹. This is compatible with the upper limit deduced above for the value of k_{12} . For the reaction of Cu_{aq}^{III} with H_2O_2 , $k = 6 \times 10^5$ dm³ mol⁻¹ s⁻¹ was reported.²⁸ This reaction can be compared with reaction (15), included in our mechanism to account for the dependence of R(HCHO)on H_2O_2 concentration. Although the products from reaction of Cu_{aq}^{III} with H_2O_2 are not known, it is unlikely that a product would be capable of chain-propagation in the $Cu_{aq}^{+} + H_2O_2 + CH_3OH$ reaction, so reaction of Cu_{aq}^{III} with H_2O_2 would act as a termination step, as we propose for reaction (15).

The lifetime of the Cu^{III}_{aq} species formed by pulse radiolysis decreased with decreasing pH, and it was suggested²⁸ that Cu^{III}_{aq} dissociates to give OH by the reverse of reaction (16), the extent of dissociation increasing with decreasing pH. In the Cu⁺_{aq} + H₂O₂ + CH₃OH reaction, R(HCHO) was dependent on pH at constant H₂O₂ concentration (table 4). We have considered, therefore, the possibility of a change in mechanism with pH, from the one, discussed above, involving Cu^{III}_{aq} at pH > 4, to one involving OH as intermediate at lower pH. The OH mechanism might be expected to dominate at pH 3, where the pulse radiolysis results have been interpreted²⁸ as indicating that Cu^{IIII}_{aq} is largely dissociated to OH⁺. However, the observed linear dependence of the HCHO yield on radiation dose and of R(HCHO) on [CH₃OH]^{1/2} (fig. 2) at pH 3, are not compatible with the formation of OH⁺ by reaction (9), for the same reasons as advanced above for the results at pH > 4. Inclusion of the reverse of reaction (16) does not change this conclusion, since reaction (5) is fast compared with reaction (16) at the CH₃OH concentrations used. At pH < 3, the relatively high value of R(HCHO) and rapid

consumption of H_2O_2 made it difficult to measure the initial value in our system and so determine the precise dependence of R(HCHO) on $[CH_3OH]$ under these conditions. However, even at pH < 1, there were indications, from both the dependence of HCHO yield on dose and of R(HCHO) on CH_3OH concentration, that freely diffusing OH⁺ is not formed.

The conclusion²⁸ that reaction (-16) occurs in the pulse radiolysis system was based mainly on the observation that the relative values of the rate constants, for reaction of the transient species with various solutes, were similar to those of OH⁺. This evidence is not unequivocal since it is possible that Cu_{aq}^{III} reacts with reducing solutes with relative rate constant values similar to those of OH⁺. If so, the different species can only be distinguished by very accurate measurements. As pointed out,²⁸ there are practical difficulties in deriving rate constant values from the pulse radiolysis data. In particular, the decay of Cu_{aq}^{III} , following the radiation pulse, is not due to a single reaction, and allowance must be made for the reaction of Cu_{aq}^{III} with Cu_{aq}^{I} . The concentration of Cu_{aq}^{H} immediately after the pulse, and therefore the contribution on the reaction of Cu_{aq}^{III} with Cu_{aq}^{I} , increases with decreasing pH. With some of the solutes studied, including CH_3OH and H_2O_2 , the matter is further complicated by reactions of intermediates produced by the reaction of the oxidising species with the solute.

pH Dependence of the HCHO Yield

There is evidence from pulse-conductivity experiments²⁹ that Cu_{aq}^{III} , produced by addition of OH[•] radicals to Cu_{aq}^{2+} , exists different acid-base forms:

$$Cu_{aq}^{3+} \rightleftharpoons Cu(OH)^{2+} \rightleftharpoons Cu(OH)^{+}_{2} \rightleftharpoons Cu(OH)_{3}$$

with $pK_a < 3.5$ for Cu(OH)²⁺ and $pK_a = 4-6$ for Cu(OH)². Assuming that the reactive intermediate formed by the Cu⁺_{aq} + H₂O₂ + CH₃OH reaction is Cu^{III}_{aq}, the rates of reactions (12) and (13) involving this intermediate might be expected to depend on the extent of its protonation. This may provide an explanation for the dependence of R(HCHO) on pH (table 4), although, with at least three competing reactions in the chain mechanism, each of which could be pH-dependent, the system is obviously complicated.

In an attempt to find out if the relative rates of reactions (12) and (13) depend on pH, we measured the HCHO radiation yield from $Cu_{aq}^{2+}+CH_3OH$ solutions, in the absence of H_2O_2 , at high $[Cu_{aq}^{2+}]/[CH_3OH]$ ratio (table 3). Under these conditions, reactions (5) and (6) are negligible compared with reactions (16) and (7) respectively, and it can be assumed that radiolysis gives Cu_{aq}^{III} and Cu_{aq}^+ . For the conditions given in table 3, the yields of these species, formed by reaction of radiation-produced OH⁺, H⁺ e_{aq}^- and H_2O_2 , are calculated from:

$$G(\operatorname{Cu}_{\operatorname{aq}}^{\operatorname{III}}) = G(\operatorname{OH}^{\cdot}) + f(\operatorname{N}_{2}\operatorname{O}) G(\operatorname{e}_{\operatorname{aq}}^{-})$$
$$G(\operatorname{Cu}_{\operatorname{aq}}^{+}) = G(\operatorname{H}^{\cdot}) + [1 - f(\operatorname{N}_{2}\operatorname{O})] G(\operatorname{e}_{\operatorname{aq}}^{-})$$

where $f(N_2O) = k_2[N_2O]/(k_2[N_2O] + k_4[H^+] + k_3[Cu_{aq}^{2+}])$ is the fraction of e_{aq}^- reacting with N₂O.

The yield of HCHO will depend on whether Cu_{aq}^{III} reacts with CH_3OH [reaction (12)] or with Cu_{aq}^+ [reaction (13)] since only the former reaction leads to HCHO [*via* reaction (8)]. Thus, if reaction (13) predominates, each Cu_{aq}^+ , formed either by reaction of radiation-produced H[•] and e_{aq}^- or by reaction (8), removes one Cu_{aq}^{III} by reaction (13), giving a predicted $G(HCHO) = [G(Cu_{aq}^{III}) - G(Cu_{aq}^+)]/2$ and $G(Cu_{aq}^+)_{net} = 0$. This appears to be the situation at pH > 4.8, where the observed HCHO yield (table 3) is close to the predicted value, $G(HCHO) = 0.1 \ \mu mol \ J^{-1}$. On the other hand, if reaction (13) is negligible, the predicted yields are

$$G(\text{HCHO}) = G(\text{Cu}_{\text{aq}}^{\text{III}}) + G(\text{H}_2\text{O}_2)$$
$$G(\text{Cu}_{\text{aq}}^+)_{\text{net}} = G(\text{Cu}_{\text{aq}}^{\text{III}}) + G(\text{Cu}_{\text{aq}}^+).$$

and

Reaction of Aquacopper(1) with Hydrogen Peroxide

[It is assumed that the radiation-produced H_2O_2 (molecular yield) will undergo reaction (11) under these circumstances]. This fits the results at $pH \leq 3$ with predicted yields, G(HCHO) = 0.45, $G(\text{Cu}_{\text{aq}}^+)_{\text{net}} = 0.64 \,\mu\text{mol J}^{-1}$ close to the measured values (table 3). The results suggest, therefore, that reaction (12) competes more effectively with reaction (13) as the pH is decreased, reaction (13) becoming negligibly slow at $pH \leq 3$. This can possibly be explained in terms of increasing protonation of the Cu^{III} species. The consequent increase in positive charge may decrease the rate of the reaction with the positively charged Cu_{aq}^{+} ion, but may have much less influence on the rate of reaction with a neutral species such as CH₃OH. The conclusion that reaction (13) is predominant at pH 5.4 is in accord with our value of $k_{12}/k_{13} = 3 \times 10^{-4}$, deduced from the kinetics of the chain reaction in the $Cu_{aq}^+ + H_2O_2 + CH_3OH$ system at pH > 4, where reaction (13) is assumed to be the main termination reaction. However, if the ratio k_{12}/k_{13} increases significantly between pH 5 and pH 3, the relatively small increase in R(HCHO) over this pH range (table 4) implies that reaction (13) is not the main chain-termination reaction at the lower pH. It is possible that the ratio k_{14}/k_{12} increases with decreasing pH²⁸ making reaction (15) the main termination reaction at low pH. The observed decrease in R(HCHO) with increasing H_2O_2 concentration at low pH (table 6), perhaps lends support to this conclusion although a detailed interpretation of the kinetics of the system in the lower pH region cannot be given at present.

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