

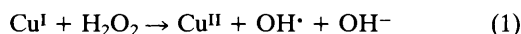
Reaction of the Aquocopper(I) Ion with Hydrogen Peroxide: Evidence against Hydroxyl Free Radical Formation

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Kinetic evidence supports the formation of a copper(III) species, rather than the hydroxyl free radical, when the aquocopper(I) ion reacts with hydrogen peroxide in aqueous solution.

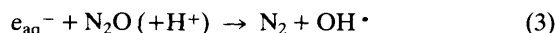
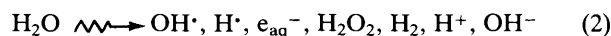
The reaction of the aquocopper(I) ion with H_2O_2 is involved in a variety of processes induced by O_2^- *in vitro*, including depolymerization of synovial fluid,¹ cytotoxicity,² and oxidative degeneration of DNA³ as well as in copper-catalysed epoxidation and hydroxylation processes.⁴ We present here evidence that has led us to question the validity of the assumption commonly made,³⁻⁶ that the OH free radical is formed by reaction (1). Our experimental findings are interpreted in terms of the formation of a Cu^{III} species by reaction of H_2O_2 with the Cu^{I} ion and some of the reactions of this Cu^{III} intermediate are discussed.



The method used to test if the OH^\bullet radical is a product of reaction (1) involved investigation of the γ -ray induced oxidation of methanol to formaldehyde in aqueous solutions containing hydrogen peroxide and aquocopper(II) ions. Under the conditions used, where the oxidation occurs as a chain reaction involving reaction of Cu^{I} ions with H_2O_2 as a propagation step, it is possible to test if the reaction kinetics are consistent with the assumption that this propagation step produces the OH^\bullet radical to act as chain carrier.

Aqueous solutions containing methanol ($0.1\text{--}2 \text{ mol dm}^{-3}$), copper(II) sulphate ($1\text{--}2 \times 10^{-3} \text{ mol dm}^{-3}$), and H_2O_2 ($0\text{--}5 \times 10^{-3} \text{ mol dm}^{-3}$), saturated with nitrous oxide gas (*ca.* $2 \times 10^{-2} \text{ mol dm}^{-3}$), were irradiated with γ -rays (Co-60, dose rate = $0.2\text{--}0.8 \text{ Gy s}^{-1}$). The HCHO yield was measured⁷ immediately after irradiation. The extent of a relatively slow thermal reaction yielding HCHO in the absence of radiation was minimised by introducing the H_2O_2 immediately before, and acidifying immediately after, exposure. Radiation yields given, which are initial values taken from linear yield-dose plots, have been corrected for the HCHO yield in the unirradiated control (<10% of the radiation yield).

In γ -irradiated, dilute aqueous solutions, reactions are initiated by the reactive species produced by the radiation-induced water decomposition process, equation (2).⁸ In our system, in the absence of H_2O_2 , the reactions (3)–(7) occur subsequently.⁸

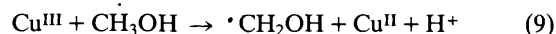


In the absence of added H_2O_2 , the observed yield of HCHO, $G(\text{HCHO}) = 0.64 \mu\text{mol J}^{-1}$ is consistent with the yield expected from the known radiation yields of the primary free radicals.⁸

With H_2O_2 present, the yield of HCHO was significantly increased to values that showed that a chain reaction occurred. The chain length is equal to $G(\text{HCHO})/G_i$, where $G_i = G(\text{OH}^\bullet) + G(e_{\text{aq}}^-) + G(\text{H}^\bullet) \approx 0.68 \mu\text{mol J}^{-1}$ is the yield of initiating radicals. The yield was markedly dependent on the pH {*e.g.*, for $[\text{CH}_3\text{OH}] = 1.0$, $[\text{H}_2\text{O}_2] = 0.003$, and $[\text{Cu}^{\text{II}}] = 0.001 \text{ mol dm}^{-3}$, $G(\text{HCHO})$ decreased from 120 to $10 \mu\text{mol J}^{-1}$ over the range $\text{pH} = 0.8\text{--}5.4$ }. At constant pH, $G(\text{HCHO})$ was directly proportional to $[\text{dose rate}]^{-1/2}$ and to $[\text{CH}_3\text{OH}]^{1/2}$. The dependence of $G(\text{HCHO})$ on $[\text{H}_2\text{O}_2]$ was complex, increasing with increasing $[\text{H}_2\text{O}_2]$ at $\text{pH} = 5.3$ but decreasing with increasing $[\text{H}_2\text{O}_2]$ at $\text{pH} < 4$. Over the range of conditions studied, $G(\text{HCHO})$ was independent of the Cu^{II} ion concentration. The maximum measured chain length was *ca.* 225. There was no evidence that significant concentrations of Cu^{I} products accumulated during the reaction. No chain production of HCHO was apparent when small concentrations of O_2 (*ca.* $10^{-4} \text{ mol dm}^{-3}$) were present.

If reaction (1) occurs in this system, production of HCHO by a chain process, propagated by reactions (1), (4), and (7), would be expected. For this mechanism, the dependence of $G(\text{HCHO})$ on methanol concentration would imply chain termination by the OH^\bullet free radical combination reaction. Taking reported values⁹ for the rate constants of this termination and of the propagation reaction (4), with dose rate = 0.8 Gy s^{-1} , $[\text{CH}_3\text{OH}] = 1.0 \text{ mol dm}^{-3}$, the expected chain length would be greater than the maximum observed by a factor of *ca.* 10^5 . Furthermore, this mechanism does not provide any explanation for the observed dependence of $G(\text{HCHO})$ on pH and on the H_2O_2 concentration.

As an alternative mechanism, we suggest the Cu^{I} ion reacts with hydrogen peroxide to give a species, formally Cu^{III} , that can react either with methanol to propagate, or with the Cu^{I} ion to terminate, the chain reaction.



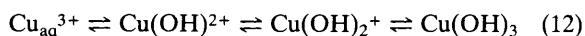
Assuming a mechanism for this chain reaction with initiation by reactions (2) to (6), propagation by reactions (7), (8), and (9) and termination by reaction (10), and making the steady-state approximation, equation (11) is obtained for $G(\text{HCHO})$ where $D = \text{dose rate}$.

$$G(\text{HCHO}) = 0.75G_i + \{k_8k_9[\text{CH}_3\text{OH}][\text{H}_2\text{O}_2]/2k_{10}D\}^{1/2} \quad (11)$$

This is consistent with the observed linear dependence of $G(\text{HCHO})$ on $[\text{CH}_3\text{OH}]^{1/2}$ and $(\text{dose rate})^{-1/2}$. The mechanism is also compatible with our results in that it implies a low stationary concentration of Cu^{I} ions, a chain length independent of the Cu^{II} ion concentration, and effective termination by oxygen, which reacts rapidly with Cu^{I} species. The

observed complex dependence of $G(\text{HCHO})$ on $[\text{H}_2\text{O}_2]$ is not explained by this mechanism alone but possibly indicates that, under certain conditions, the Cu^{III} intermediate can react with H_2O_2 to terminate the chain.

The formation of a Cu^{III} species by a reaction of hydrogen peroxide with Cu^{I} has previously been suggested.¹⁰ Furthermore, there is evidence that an aquo Cu^{III} species is produced by reaction of OH^\bullet radicals with Cu^{II} ions¹¹ and exists in forms linked by the protolytic equilibria in equation (12).^{8,12} There is considerable uncertainty associated with the values of the acid dissociation constants for these species¹² but it is probable that $\text{p}K_{\text{a}} < 3.5$ for $\text{Cu}(\text{OH})_2^{2+}$ and $\text{p}K_{\text{a}} = 4-6$ for $\text{Cu}(\text{OH})_2^+$. The dependence of chain length on pH in our system can be accounted for if it is assumed that the value of the rate constant ratio, k_9/k_{10} , depends on the extent of protonation of the Cu^{III} species.



In the presence of certain ligands capable of complexing copper ions, including amino acids, oxalate, and 1,10-phenanthroline, the chain length in the irradiated Cu^{II} -hydrogen peroxide-methanol system was significantly decreased. This may be because of a decrease in the rate constant ratio, k_9/k_{10} , when the Cu ions are complexed, with a consequent decrease in the efficiency with which methanol is oxidised. Alternatively, the complexed Cu^{III} species may react by oxidation of the attached ligand, rather than by dehydrogenation of methanol. The latter appears to be the case, at

least with glycine and α -alanine as ligands, where we have observed the formation of ammonia as a product in yields that indicate that ligand oxidation is a significant process.

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