Formation of Epoxides in the Oxidation of β-Hydroxyalkyl Radicals by Copper(II) in Aqueous Solution

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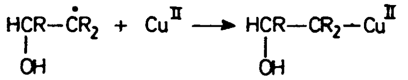
Summary High yields of epoxides are produced when β-hydroxyalkyl radicals are oxidised by copper(II) ion in aqueous solution at pH 3—6; kinetic data show that interaction of the radical with copper(II) ion is rate controlling.

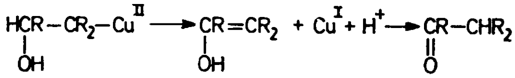
KOCHI *et al.*[1] have shown that the oxidation of alkyl radicals by Cu^{II} generally proceeds *via* the formation of a radical–Cu^{II} complex which can then undergo either β-proton elimination to form an alkene, or electron transfer to form a carbonium ion. For β-hydroxyalkyl radicals the reaction sequence would be (1) followed by (2) or (3) to produce ketone or glycol respectively. Walling and Kato[2] found evidence only for glycol production in the oxidation of β-hydroxyalkyl radicals by simple hydrated copper(II) ion in aqueous solution at pH 0·82. They also concluded that these radicals are not oxidised by iron(III) ion.

We have found, however, in two sets of experiments, that the major product of the oxidation of β-hydroxyalkyl radicals by copper(II) ion in aqueous solution at higher pH (3—6) is in fact epoxide, presumably through reaction (4).

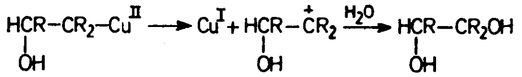
Firstly, when Fenton's reagent was added to an aqueous solution of 2 mmol dm^{-3} of copper(II) ion and 0·55 mol dm^{-3} of propan-2-ol at pH 3·7—4·0, acetone and propylene oxide were produced in the ratio 6 : 1. This corresponds closely to the ratio in which α- and β-hydroxyisopropyl radicals are generated when OH reacts with propan-2-ol.[3] In the absence of copper(II) ion no propylene oxide was detected.



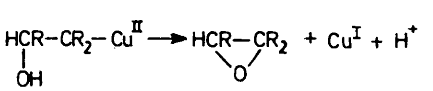
$$\underset{\mathrm{OH}}{\mathrm{HCR}}-\dot{\mathrm{C}}\mathrm{R_2} + \mathrm{Cu^{II}} \longrightarrow \underset{\mathrm{OH}}{\mathrm{HCR}}-\mathrm{CR_2}-\mathrm{Cu^{II}} \qquad (1)$$



$$\underset{\mathrm{OH}}{\mathrm{HCR}}-\mathrm{CR_2}-\mathrm{Cu^{II}} \longrightarrow \underset{\mathrm{OH}}{\mathrm{CR}}=\mathrm{CR_2} + \mathrm{Cu^{I}} + \mathrm{H^+} \longrightarrow \underset{\underset{\mathrm{O}}{\|}}{\mathrm{CR}}-\mathrm{CHR_2} \qquad (2)$$



$$\underset{\mathrm{OH}}{\mathrm{HCR}}-\mathrm{CR_2}-\mathrm{Cu^{II}} \longrightarrow \mathrm{Cu^{I}} + \underset{\mathrm{OH}}{\mathrm{HCR}}-\overset{+}{\mathrm{C}}\mathrm{R_2} \xrightarrow{\mathrm{H_2O}} \underset{\mathrm{OH}}{\mathrm{HCR}}-\mathrm{CR_2OH} \qquad (3)$$



$$\underset{\mathrm{OH}}{\mathrm{HCR}}-\mathrm{CR_2}-\mathrm{Cu^{II}} \longrightarrow \mathrm{HCR}\underset{\mathrm{O}}{\diagdown\;\diagup}\mathrm{CR_2} + \mathrm{Cu^{I}} + \mathrm{H^+} \qquad (4)$$

Secondly, when aqueous solutions of 10 mmol dm^{-3} of $\mathrm{Cu(ClO_4)_2}$ saturated with ethylene at pH 3 or 6 were γ-irradiated, ethylene oxide was produced with an initial G-value of 3·3. This is approximately equal to $G(\mathrm{OH}) + G(\mathrm{H_2O_2})$ in this system in which OH reacts with ethylene to form β-hydroxyethyl radicals exclusively, and indicates that there is a contribution to the total yield of OH from reaction (5). When 40 mmol dm^{-3} of methanol was added to the system at pH 3 G(epoxide) was decreased to *ca.* 1 which is consistent with the expected competition between methanol and ethylene for OH.

$$\mathrm{Cu^{I}} + \mathrm{H_2O_2} \rightarrow \mathrm{Cu^{II}} + \cdot\mathrm{OH} + \mathrm{OH^-} \qquad (5)$$

The participation of reaction (5) in the formation of epoxide was confirmed by adding 3·5 mmol of $\mathrm{H_2O_2}$ to an irradiated solution (pH 3) containing 0·13 mmol of $\mathrm{Cu^{I}}$ complexed with ethylene which resulted in a further 0·3 mmol of ethylene oxide being produced. In this case a chain reaction is set up, since $\mathrm{Cu^{I}}$ is regenerated in reaction (4), which proceeds until all the $\mathrm{Cu^{I}}$ is consumed. The major chain terminating step is probably reaction (6) which has a rate constant of *ca.* 2×10^{10} dm^3 mol^{-1} s^{-1}.[4] The formation of ethylene oxide in this case was only suppressed

$$\cdot\mathrm{CH_2CH_2OH} + \mathrm{Cu^{I}} \rightarrow \mathrm{CH_2{=}CH_2} + \mathrm{Cu^{II}} + \mathrm{OH^-} \qquad (6)$$

by methanol when the latter was present in a large excess so that it reacted with virtually all the hydroxyl radicals to produce hydroxymethyl radicals. This result is entirely consistent with the mechanism of epoxide formation described by reactions (5), (1), (4), and (6) if hydroxymethyl radicals only participate in the chain propagating reaction (7).

$$\cdot\mathrm{CH_2OH} + \mathrm{Cu^{II}} \rightarrow \mathrm{Cu^{I}} + \mathrm{CH_2O} + \mathrm{H^+} \qquad (7)$$

The rate of formation of $\mathrm{Cu^{I}}$ in the oxidation of β-hydroxyalkyl radicals by $\mathrm{Cu^{II}}$ was measured by pulse radiolysis.[4] It was proportional to $[\mathrm{Cu^{II}}]$, confirming that reaction (1) is rate controlling.[1] We obtained values of k_1 of 2×10^7 dm^3 mol^{-1} s^{-1} for β-hydroxyethyl radicals and 3×10^6 dm^3 mol^{-1} s^{-1} for β-hydroxyisobutyl radicals. These values are consistent with greater steric hindrance to the formation of the metal–carbon bond in the latter case.

The formation of epoxides from alkenes by a route involving hydroxyl radicals suggests that a similar mechanism could operate in enzymic epoxidation.[5] Hydroxyl radicals as intermediates in enzymic hydrocarbon oxidations[6] would also provide explanations for the observed reactions without the need to postulate novel species.

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