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Formation of Epoxides in the Oxidation of β-Hydroxyalkyl Radicals by Copper(11) 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 Kato² 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.

$$\begin{array}{ccc} HCR-\dot{CR}_{2} + Cu^{II} & \longrightarrow & HCR-CR_{2}-Cu^{II} & (1) \\ I & I & I \\ OH & OH & OH \end{array}$$

$$\begin{array}{ccc} HCR - CR_2 - Cu^{II} \longrightarrow CR = CR_2 + Cu^{I} + H^{\dagger} \longrightarrow CR - CHR_2 \quad (2) \\ I & I \\ OH & OH & O \end{array}$$

$$\begin{array}{c} HCR - CR_2 - C_u^{II} - \cdots > C_u^{II} + HCR - CR_2 \xrightarrow{H_2O} HCR - CR_2OH \quad (3) \\ I \\ OH \\ OH \\ OH \\ OH \end{array}$$

$$HCR-CR_2-Cu^{II} \rightarrow HCR-CR_2 + Cu^{I} + H^{+}$$
(4)

Secondly, when aqueous solutions of 10 mmol dm^{-3} of $Cu(ClO_4)_2$ saturated with ethylene at pH 3 or 6 were γ irradiated, ethylene oxide was produced with an initial Gvalue of 3.3. This is approximately equal to G(OH) + $G(H_2O_2)$ 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.

$$Cu^{I} + H_{2}O_{2} \rightarrow Cu^{II} + OH + OH^{-}$$
(5)

The participation of reaction (5) in the formation of epoxide was confirmed by adding $3.5 \text{ mmol of } H_2O_2$ to an irradiated solution (pH 3) containing 0.13 mmol of CuI

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complexed with ethylene which resulted in a further 0.3mmol of ethylene oxide being produced. In this case a chain reaction is set up, since Cu^{I} is regenerated in reaction (4), which proceeds until all the Cu^{I} is consumed. The major chain terminating step is probably reaction (6) which has a rate constant of ca. $2 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1.4}$ The formation of ethylene oxide in this case was only suppressed

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

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

The rate of formation of Cu^{I} in the oxidation of β hydroxyalkyl radicals by CuII was measured by pulse radiolysis.⁴ It was proportional to [Cu^{II}], confirming that reaction (1) is rate controlling.¹ We obtained values of k_1 of 2×10^7 dm³ mol⁻¹ s⁻¹ for β -hydroxyethyl radicals and 3×10^6 dm³ 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 oxidations⁶ would also provide explanations for the observed reactions without the need to postulate novel species.

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- ⁵ D. M. Jerina, Chem. Tech., 1973, 120.