Formation of Semidione Radicals on Production of 1,2-Dihydroxyalkyl Radicals in the Presence of Peroxides in Basic Solution. An Electron Spin Resonance Study

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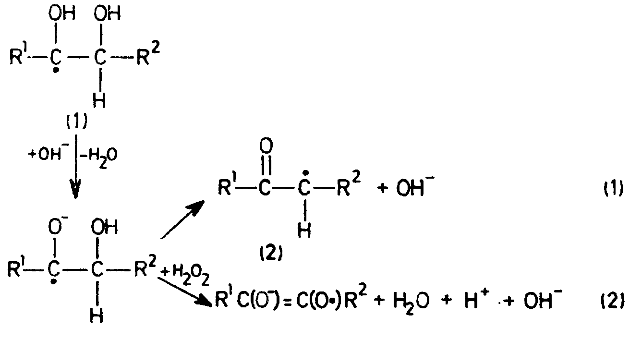
Summary In basic solution containing hydrogen peroxide or organic peroxides, 1,2-dihydroxyalkyl radicals are converted into semidione radical anions in low yield.

DURING investigations on the generality of the base-catalysed elimination of water[1,2] from 1,2-dihydroxyalkyl radicals (**1**) to yield β-oxoalkyl radicals (**2**) [reaction (1)], we have observed, using the *in situ* photolysis–e.s.r. method,[3] in addition to (**2**), semidione radical anions (**3**) and α-carboxyalkyl radical anions (**4**) (Figure) when the alkaline solutions contained H_2O_2. At a constant rate of production of (**1**) using triplet acetone as the H-abstractor and constant pH the amplitude of the signals due to (**3**) increased with increasing $[H_2O_2]$ from *ca.* 1 mM to a saturation level at *ca.* 100 mM $[H_2O_2]$. H_2O_2 had practically no effect on the amplitude of the signals due to (**2**). At constant $[H_2O_2]$ the amount of (**3**) increased with increasing pH from pH *ca.* 7·5 and to a saturation level at pH *ca.* 9—9·5. The pH dependence of the amount of (**4**) was less reproducible. On multiple u.v. irradiations of solutions (substrate conversion per cycle $\leqslant 1\%$) the amount of (**3**) remained unchanged which suggests that radicals of type (**3**) are not derived from secondary products. When H_2O_2 was replaced by $K_2S_2O_8$ (5—100 mM), radicals of type (**4**) were not detected and radicals (**3**) were observed in stationary concentrations lower by a factor of *ca.* 5 compared to corresponding solutions containing H_2O_2. One of the isomers[4] (probably *cis*) of (**3a**) could also be obtained by producing (**1a**) in alkaline Bu^tOH as solvent, with triplet acetone as the H-abstractor and H_2O_2, $Bu^tO{\cdot}OBu^t$, or $PhCH_2O{\cdot}OCH_2Ph$ as oxidising agent.



(3) (*cis* and *trans*)

a; $R^1 = R^2 = H$
b; $R^1 = H, R^2 = CH_2OH$
c; $R^1 = CH_2OH, R^2 = H$
d; $R^1 = H, R^2 = Me$
e; $R^1 = Me, R^2 = H$

$R\dot{C}HCO_2^-$ R = H, Me, or CH_2OH
(**4**)

FIGURE. E.s.r. spectra recorded during photolysis of H_2O_2 (0·16 M) in the presence of ethylene glycol (1·6 M) at pH 9·6 and 3 °C. Modulation amplitude 0·01 mT (insert 0·0063 mT), microwave power 1 mW. Under these conditions lines from $\cdot CH_2CHO$ are invisible.

On the basis of the pH-dependence of the formation of (**3**) and considering that alcohol radicals are characterised by pK^a values between 10·7 and 12·2,[5] it is suggested that the semidiones are produced by the reaction of deprotonated (**1**) with H_2O_2 [reaction (2)]. As judged by the insignificant reduction of the stationary concentration of (**2**) on addition of H_2O_2, reaction (2) does not compete very efficiently with reaction (1). This conclusion is in agreement with an estimated[1] first-order rate constant of $10^6\ s^{-1}$ for reaction (1). A reaction analogous to (2) has been proposed by Norman *et al.*[6] to rationalise the production of semiquinones observed on reaction of ·OH with phenol. The semidiones could also arise from α-hydroxyoxo-compounds, formed[7] by reaction of un-ionised (**1**) with H_2O_2, followed by an H-abstraction step. In the ethylene glycol and glycerol systems (**1a**—**c**) this mechanism was tested by adding 1—50 mM of glycolaldehyde or glyceraldehyde, respectively, to the solution under photolysis. The possibility of destruction of the aldehydes by reaction[7] with H_2O_2 before reaching the e.s.r. cell was minimised by mixing the reactants immediately before entering the cell. In agreement with previous findings,[8] no increase in the stationary concentration of (**3**) was observed. Furthermore, on the basis of this mechanism, a change in the stationary concentration of (**3**) should occur around pH 4·4 since the pK_a values of (**3**) are close to 4·4.[9] Experimentally, semidiones were not observed below pH 7·5.

There is also the possibility that radicals (**3**) are formed from (**2**) by reaction with H_2O_2. This was tested by generating (**2**) from non-glycol substrates. (**2a**) was produced from 2-chloroethanol[10] in phosphate buffer (pH 7)[11] and (**2e**) was produced from acetone at pH 9·5. In solutions containing 100 mM of H_2O_2, no evidence was found for the formation of (**3a**) or (**3e**), respectively.

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