Introduction

Hydroxy radicals add to C-C double bonds thereby creating a carbon-centered radical (e.g. reaction (1)). In the presence of oxygen such carbon-centered radicals are converted into the corresponding peroxy radicals (e.g. reaction (2)). Both reactions are very fast, i.e. nearly diffusion-controlled.

\[
\begin{align*}
\cdot \text{OH} + \text{CH} = \text{CH}_2 & \rightarrow \text{HO} - \text{CH} = \text{CH}_2 \quad \text{(1)} \\
\text{HO} - \text{CH} = \text{CH}_2 + \text{O}_2 & \rightarrow \text{HO} - \text{CH} = \text{CH}_2 - \text{O}_2 \quad \text{(2)}
\end{align*}
\]

Our interest in this type of reaction arose from the fact that upon radiolysis of DNA in aqueous solution the major part of OH radicals add to the double bonds of the bases, and in the first stages reactions of the type (1) and (2) have to be assumed. With DNA and even with the nucleobases the subsequent reactions are rather complex (cf. uracil [1]). One could expect that the functional prototype, the \(\beta\)-hydroxyethylperoxyl radical, gives some information about the reactions to be considered in the more complex systems.

Some reports exist on products from the \(\beta\)-hydroxyethylperoxyl radical in aqueous solution [2–4], however, Clay et al. [3] suggested at the time that it was premature to put forward a mechanism, and also the latter study [4] did not provide enough experimental material from which mechanistic conclusions could have been drawn. A new investigation is thus justified. Preceding the present work, another simple \(\beta\)-hydroxyethylperoxyl radical has been studied in detail, namely the peroxy radical derived from \(\tau\)-butanol [5]. A comparison between these two systems will allow us to assess the effect of alkyl substituents in the subsequent reactions.

The radiolysis of a mixture (5:4:1) of ethylene, nitrous oxide, and oxygen in water provides a relatively clean source of \(\beta\)-hydroxyethylperoxyl radicals. Under such conditions the solvated electrons formed by the radiolysis of water (reaction (3)) are converted by the \(\text{N}_2\text{O}\) into OH radicals (reactions (4)) which add to the ethylene (reaction (1)). At the given conditions the radiation-chemical yield \(G^*\) of the \(\beta\)-hydroxyethyl radicals will be 5.4 [6]. According to reported rate constants [7] the small amount of H atoms formed under our conditions \((G(\text{H}) = 0.55)\) will be scavenged both by ethylene (2/3) (reactions (5)) and oxygen (1/3) (reaction (6)). The ethylene-

* The \(G\) value is defined as number of molecules formed per 100 eV of absorbed energy.

\(\beta\)-Hydroxyethylperoxyl Radicals: A Study of the \(\gamma\)-Radiolysis and Pulse Radiolysis of Ethylene in Oxygenated Aqueous Solutions

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Peroxyl Radicals, Oxyl Radicals, Pulse Radiolysis, Ethylene, Reaction Kinetics

Hydroxy radicals (and H atoms) generated in the radiolysis of \(\text{N}_2\text{O}\)-containing water add to ethylene forming \(\beta\)-hydroxyethyl radicals (and ethyl radicals). In the presence of oxygen these are converted into the corresponding peroxy radicals which decay bimolecularly \((k = 2 \times 10^8 \text{ M}^{-1} \text{s}^{-1})\) as measured by pulse radiolysis. The major products (\(G\) values in brackets) are glycolaldehyde (3.3), formaldehyde (1.6), ethylene glycol (0.8), acetaldehyde (0.5), organic peroxodic material (0.5), and hydrogen peroxide (2.4) (dose rate 0.26 Gy s\(^{-1}\), pH 5.6). A material balance has been obtained with respect to the primary water radicals (6.0) and oxygen uptake (4.8). The products and their yields can be accounted for if in the rate determining step a tetroxide is formed which decomposes via three major pathways leading to: (i) \(\text{H}_2\text{O}_2\) and two molecules of glycolaldehyde (ca. 45%), (ii) \(\text{O}_2\), glycolaldehyde and ethylene glycol (ca. 30%), and (iii) \(\text{O}_2\), two molecules of formaldehyde and two \(\text{CH}_2\text{OH}\) radicals (ca. 15%). A 1.2-H shift of intermediate oxyl radicals is unimportant in this system.

\[
\begin{align*}
\cdot \text{OH} + \text{CH} = \text{CH}_2 & \rightarrow \text{HO} - \text{CH} = \text{CH}_2 \quad \text{(3)} \\
\text{HO} - \text{CH} = \text{CH}_2 + \text{O}_2 & \rightarrow \text{HO} - \text{CH} = \text{CH}_2 - \text{O}_2 \quad \text{(4)}
\end{align*}
\]

Some reports exist on products from the \(\beta\)-hydroxyethylperoxyl radical in aqueous solution [2–4], however, Clay et al. [3] suggested at the time that it was premature to put forward a mechanism, and also the latter study [4] did not provide enough experimental material from which mechanistic conclusions could have been drawn. A new investigation is thus justified. Preceding the present work, another simple \(\beta\)-hydroxyethylperoxyl radical has been studied in detail, namely the peroxy radical derived from \(\tau\)-butanol [5]. A comparison between these two systems will allow us to assess the effect of alkyl substituents in the subsequent reactions.

The radiolysis of a mixture (5:4:1) of ethylene, nitrous oxide, and oxygen in water provides a relatively clean source of \(\beta\)-hydroxyethylperoxyl radicals. Under such conditions the solvated electrons formed by the radiolysis of water (reaction (3)) are converted by the \(\text{N}_2\text{O}\) into OH radicals (reactions (4)) which add to the ethylene (reaction (1)). At the given conditions the radiation-chemical yield \(G^*\) of the \(\beta\)-hydroxyethyl radicals will be 5.4 [6]. According to reported rate constants [7] the small amount of H atoms formed under our conditions \((G(\text{H}) = 0.55)\) will be scavenged both by ethylene (2/3) (reactions (5)) and oxygen (1/3) (reaction (6)). The ethylene-

* The \(G\) value is defined as number of molecules formed per 100 eV of absorbed energy.
derived radicals are converted into the corresponding peroxyl radicals (reactions (2) and (7)).

\[ \text{H}_2\text{O} \xrightarrow{\text{ionising radiation}} \cdot \text{OH}, \cdot \text{H}, e_{\text{aq}}, \text{H}^+, \text{H}_2\text{O}_2, \text{H}_2 \]

(3)

\[ e_{\text{aq}} + \text{N}_2\text{O} \rightarrow \cdot \text{OH} + \text{N}_2 + \cdot \text{OH}^- \]

(4)

\[ \text{H}^+ + \text{CH}_2=\text{CH}_2 \rightarrow \text{CH}_3\cdot \text{CH}_2 \]

(5)

\[ \text{H}^+ + \text{O}_2 \rightarrow \text{HO}_2 \rightarrow \text{H}^+ + \text{O}_2 \]

(6)

\[ \text{CH}_3\cdot \text{CH}_2 + \text{O}_2 \rightarrow \text{CH}_3\cdot \text{CH}_2\cdot \text{O}_2 \]

(7)

Thus the \( \beta \)-hydroxyethylperoxyl radicals make up \( \approx 91\% \) of the total radical yield, and the small amounts of ethylperoxyl radicals (ca. 6\%) and primary HO\(_2\)/HO\(_2\) (ca. 3\%) can be neglected for most purposes.

**Results**

Glycolaldehyde, hydrogen peroxide, formaldehyde, ethylene glycol and acetaldehyde are the major products. There is also some organic peroxidic material. The \( G \) values of these products are given in Table I. From this table one can also see that within the limit of experimental error which is considered to be 10\%, it makes little difference whether irradiation is done at pH 5.6 or 10. At high dose rates \( G \) (formaldehyde) drops significantly. Ethylene glycol has been measured by two different methods, spectrophotometrically after conversion of ethylene glycol into formaldehyde by periodate, and directly using gas chromatography. These value differ somewhat. Preference is given to the latter, because the former method gives the sum of the directly produced formaldehyde plus that from the ethylene glycol as well as that liberated by periodate oxidation of the glycolaldehyde. Considering this, the agreement between the two methods is acceptable.

Some experiments have also been carried out with solutions saturated with ethylene/oxygen (1:1 v/v) and the major products (\( G \) values in brackets) measured: glycolaldehyde (1.5), formaldehyde (0.7), organic peroxidic material (0.6), hydrogen peroxide (2.2). It is noted that the yields of glycolaldehyde and formaldehyde drop to somewhat less than half the value obtained from \( \text{N}_2\text{O} \)-containing solutions, but that of the organic peroxidic material is enhanced.

The fate of the peroxyl radicals has been followed by pulse radiolysis using conductometric detection. This is possible in peroxyl radical reactions whenever HO\(_2\) (pK\(_a\) = 4.7) is set free or carboxylic acids are formed. In the present system of \( \text{N}_2\text{O}/\text{O}_2 \)-containing ethylene solutions at pH \( \approx 6 \) an increase in conductivity was observed which is kinetically of second-order \( (2k = (2.0 \pm 0.5) \times 10^8 \text{M}^{-1}\text{s}^{-1}) \). Although there is a small contribution from conducting transient species (\( \text{H}^+ + \text{O}_2 \)), the major part of this conductivity increase is due to a permanent acid; \( G(\text{H}^+) = 0.7 \). The formation of a permanent acid was confirmed by potentiometric titration of the pulse-irradiated solutions which gave \( G(\text{acid}) = 0.9 \). This permanent acid is mainly formic acid together with traces of glycolic acid as shown by ion chromatography. It is noted that the acid was only found at the high dose rates delivered by pulse radiolysis, but was not (or only to a very minor extent) observed under the low dose rate conditions of the 60-Co-\( \gamma \)-irradiations. In basic solutions (pH 9—10.5), a drop of conductivity was observed due to the replacement of OH\(^-\) \( (\lambda^0 = 180 \text{ M}^{-1}\text{cm}^2) \) by \( \text{O}_2^- \) \( (\lambda^0 = 65 \text{ M}^{-1}\text{cm}^2) \). The same second-order rate constant was found as observed in neutral solutions. The maximum \( G \) value for \( \text{O}_2^- \) reached is 1.1 including the prompt formation of \( \text{O}_2^- \) (\( G = 0.2 \)) from primary H atoms scavenged by \( \text{O}_2 \). No permanent acid is formed in alkaline solutions.

<table>
<thead>
<tr>
<th>Product</th>
<th>Dose rate: 0.26 Gy s(^{-1})</th>
<th>Dose rate: 7.8 Gy s(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>pH = 5.6 pH = 10</td>
<td>pH = 5.6 pH = 5.6</td>
</tr>
<tr>
<td>Glycolaldehyde</td>
<td>3.3 3.1</td>
<td>3.0 3.4</td>
</tr>
<tr>
<td>Formaldehyde</td>
<td>1.6 1.7</td>
<td>1.35 1.1</td>
</tr>
<tr>
<td>Ethylene glycol</td>
<td>0.8* (0.6) (0.5)</td>
<td>(0.6)</td>
</tr>
<tr>
<td>Organic peroxidic material</td>
<td>0.5 0.4</td>
<td>0.4</td>
</tr>
<tr>
<td>Acetaldehyde</td>
<td>0.5*</td>
<td></td>
</tr>
<tr>
<td>( \text{H}_2\text{O}_2 )</td>
<td>2.4 2.4</td>
<td>2.3 0.7</td>
</tr>
<tr>
<td>Formic acid</td>
<td>traces</td>
<td>traces</td>
</tr>
<tr>
<td>Oxygen uptake</td>
<td>4.8</td>
<td></td>
</tr>
</tbody>
</table>

* GC-measurements.

Table 1. Radiolysis of ethylene in aqueous solutions in the presence of \( \text{N}_2\text{O}/\text{O}_2 \). Products and their \( G \) values.
**Discussion**

In an earlier report [2] on the irradiation of aqueous solutions of an ethylene/oxygen mixture saturated at elevated pressures the existence of a chain reaction had been suggested. This was later shown not to be the case [3]. In the present study the ethylene has been used at much lower concentrations while the dose rates have been similar. Hence a chain reaction of any importance is not expected. The hydroxyethyl radicals (from reaction (1)) add to the ethylene rather slowly \( k = 3 \times 10^4 \text{ M}^{-1} \text{s}^{-1} \) [9], while addition to oxygen (reaction (2)) \( k(2) \approx 2 \times 10^9 \text{ M}^{-1} \text{s}^{-1} \), estimated, cf. [10]) must be much faster under our experimental conditions. A chain reaction could only proceed if the peroxy radicals formed in reaction (2) were to add to the ethylene. From the rate constant of the decay of the \( \beta \)-hydroxyethylperoxyl radicals \( 2k = 2 \times 10^8 \text{ M}^{-1} \text{s}^{-1} \) determined in the present work (see below), one arrives at a steady-state concentration of peroxy radicals of \( 2 \times 10^{-8} \text{ M} \) at a dose rate of 0.26 Gy s\(^{-1}\). At this dose rate \( G(\text{oxygen uptake}) = 4.8 \) is in conformity with the oxygen content of the products shown in the Table. This value strongly suggests that there is no chain reaction of any importance under our experimental conditions. An upper limit for the rate constant of the addition of the \( \beta \)-hydroxyethylperoxyl radicals to ethylene can be estimated by assuming that if a chain reaction exceeded 10% of the non-chain processes it would have become apparent both by product as well as by oxygen uptake measurements. Using the values for the bimolecular decay rate, the ethylene concentration, and the steady-state concentration of the \( \beta \)-hydroxyethylperoxyl radicals at the above dose rate, it is calculated that the peroxy radicals, if they add to the ethylene, must do so with a rate constant of \(<200 \text{ M}^{-1} \text{s}^{-1}\).

Because of the absence of a chain reaction the \( \beta \)-hydroxyethylperoxyl radicals are left to decay bimolecularly. A bimolecular decay of these radicals can be rationalized by the sequence of reactions shown in the scheme (reactions (8)–(18)). It is now generally accepted that in the bimolecular decay of peroxy radicals a short-lived tetroxide is formed (reaction (8)) which may revert to the peroxy radicals (reactions (9)), or decompose into the products. Two concerted mechanisms have been recognized so far. The so-called Russell mechanism leads to oxygen, glycoaldehyde and ethylene glycol (reaction (10)). The yield of glycoaldehyde is much higher than that of ethylene glycol. This can be accounted for by the other concerted reaction (reaction (11)). In competition with these two processes there is the fragmentation of the tetroxide into one molecule of oxygen and two oxyl radicals (reaction (12)). The disproportionation of these two oxyl radicals within the solvent cage (reaction (13)) leads to the same products as the Russell-mechanism. Combined (10) and (13) contribute 30% \((G = 1.6, \text{twice } G(\text{ethylene glycol}))\). The combination of the two oxyl radicals...
would lead to the corresponding peroxide (reaction (14)). Such a reaction is usually of little importance (cf. [11]), especially at low temperatures (cf. [5]). Some of the organic peroxidic material found might be due to this reaction. Moreover, there is another pathway for the oxyl radicals, namely β-fragmentation (reaction (15)). This reaction leads to the formation of some of the formaldehyde. The resulting hydroxymethyl radicals add oxygen (reaction (16)). α-Hydroxylalkyl radicals are known to eliminate HO₂⁻ (for a review see [12]). The HO₂⁻-elimination of the hydroxymethylperoxyl radical is rather slow at pH < 7 but is considerably speeded up by OH⁻ [13].

At the low dose rate experiments of the 60-Co-γ-irradiations the majority of the hydroxymethylperoxyl radicals eliminate HO₂⁻ according to reaction (17), a reaction that supplies the second half of the formaldehyde yield, but at the dose rate conditions of pulse radiolysis these radicals mainly decay bimolecularly. Their self-termination nearly exclusively leads to formic acid (reaction (18)) [14], a reaction which is equivalent to reaction (11). Although only the self-termination reaction has been depicted in the scheme, termination with the β-hydroxymethylperoxyl radical stands a good chance to lead to formic acid as well. In the pulse radiolysis experiment, G(permanent acid) was ca. 0.7 at pH 6, in good agreement with the maximum yield of 0.8 calculated from the formaldehyde yield (one half of G(CH₂O) = 1.6) under 60-Co-γ-irradiation.

At high pH the observed conductivity changes are fully accounted for by the HO₂⁻-elimination of the hydroxymethylperoxyl radical (OH⁻-induced mode of reaction (17)). This leaves practically no room for yet another source of HO₂⁻(H⁺ + O₂⁻), such as reaction (21) preceded by reactions (19) and (20).

\[
\begin{align*}
\text{HO} - \text{CH} - \text{CH}₂\text{OH} + \text{O}₂ &\rightarrow \text{HO} - \text{CH} - \text{CH}₂\text{OH} \\
\text{HO} - \text{CH} - \text{CH}₂\text{OH} + \text{O}_₂ &\rightarrow \text{HO} - \text{CH} - \text{CH}₂\text{OH} \\
\text{HO} - \text{C} - \text{CH}₂\text{OH} &\rightarrow \text{HO}_₂ + \text{CHO} - \text{CH}₂\text{OH} \\
\text{HO} - \text{C} - \text{CH}₂\text{OH} &\rightarrow \text{HO}_₂ + \text{CHO} - \text{CH}₂\text{OH}
\end{align*}
\]

The rearrangement of oxyl radicals (cf. reaction (19)) [15–18] can play a considerable role in peroxy radical chemistry in aqueous solutions [11, 19, 20].

The near absence of this process in the present system is ascribed to the effective competition by fragmentation [17] (cf. reaction (15)) facilitated by the lowering of the C–C bond energy due to the OH substituent. About 15% of the primarily formed peroxy radicals eventually decay by fragmentation (reaction (15)) (one half of G(CH₂O), cf. reactions (15)–(17)). The importance of this type of pathway is increased if the strength of the bond to be broken is further weakened by two methyl groups as in the case of the t-butanol system [5]. There the corresponding fragmentation process contributed 30% to the overall reactions. This brings up the question whether the fragmentation process is indeed a two-step mechanism (as shown in the Scheme) or whether a large proportion of the fragmentation products are formed without free oxyl radicals as intermediates, i.e. whether the tetroxide decomposes directly into oxygen, two molecules of carbonyl compounds and two alkyl radicals. A contribution of the one-step mechanism would explain somewhat better the higher yield of fragmentation in the t-butanol case than in the present one, because the bond energy of the fragmenting bond would play a role at the very early stage (compared to the other, e.g. concerted processes) rather than at the stage of the oxyl radical where competition is only possible for the 1,2-H shift (besides disproportionation and combination). Recently it has been shown that in the case of cyclopentylperoxyl radicals the (important) fragmentation route is indeed mainly such a concerted process and does not involve free oxyl radicals as intermediates [21].

Since the reaction sequence (19) to (21) has been rejected as insignificant, the excess of glycolaldehyde over ethylene glycol has to be explained. The most likely route is the concerted reaction (11). There is increasing evidence that this route can play a considerable role (cf. especially [14] but also [5, 11]). One then calculates that reaction (11) contributes 45%, i.e. it is the most important single process in the present system.

The organic peroxidic material has not been characterised in detail. It may well be due to some organic peroxy from reaction (14) but, more likely, HO₂⁻ formed from H atoms and oxygen as well as by reaction (17) might give rise to the hydroperoxide (reaction (22)).

\[
\begin{align*}
\text{HO} - \text{CH}₂ - \text{CH}₂ - \text{O}₂^- + \text{HO}_₂(H⁺ + \text{O}₂^-) &\rightarrow \\
\text{HO} - \text{CH}₂ - \text{CH}₂ - \text{OOH} + \text{O}_₂
\end{align*}
\]
The role of $\text{HO}_2/\text{O}_2^\cdot$ in the formation of hydroperoxides has first been proposed by Johnson and Weiss [22] and recently reconfirmed by additional experiments [11]. Our observation that the yield of organic peroxidic material is increased if $\text{O}_2$ becomes more abundant ($\text{O}_2^\cdot$ vs. $\text{N}_2\text{O}_2/\text{O}_2$-containing solutions) is in agreement with this interpretation.

The small amount of acetaldehyde that are observed are due to the subsequent reactions of the ethylperoxy radical formed in reactions (5) and (7).

**Experimental**

The solutions were prepared by saturating triply distilled water with a 1:1 (v/v) gas mixture of ethylene (Chemische Werke Hüls) and $\text{N}_2\text{O}/\text{O}_2$ (4:1) resulting in an ethylene concentration of $2.7 \times 10^{-3}$ M. Irradiations were carried out at room temperature ($19 \pm 2^\circ\text{C}$) at dose rates of 0.26 Gy s$^{-1}$, 7.8 Gy s$^{-1}$ (60-Co-$\gamma$) and a train of 2 $\mu$s 2.8 MeV electron pulses (2.5 Gy per pulse). Conversions were <10%.

Glycolaldehyde was determined spectrophotometrically [23] using $\varepsilon(580 \text{ nm}) = 5 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$. Formaldehyde was assayed using the acetylacetone method [24] ($\varepsilon(412 \text{ nm}) = 7700 \text{ M}^{-1}\text{cm}^{-1}$). Ethylene glycol was measured by two different methods, colorimetrically after conversion of formaldehyde by periodate [24] or gas chromatographically by direct injection of the irradiated solution on a 25 m Carbowax 20 M capillary column, temperature programmed, 65–200 $^\circ\text{C}$, 15° min$^{-1}$, carrier gas H$_2$. Total peroxide was determined iodometrically [25] ($\varepsilon(350 \text{ nm}) = 2.7 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$). Organic hydroperoxide was estimated by the same method after $\text{H}_2\text{O}_2$ had been destroyed by catalase. Gas chromatographic analysis of acetaldehyde was carried out on a 52 m OV 1 column with a 10 m Carbowax 20 M precolumn, at 85 $^\circ\text{C}$, N$_2$ at 1 mlmin$^{-1}$. Total acid was determined by potentiometric titration against 0.01 M NaOH. Formic acid was detected by high-performance ion chromatography using a Dionex ion chromatograph equipped with HPIC AS 4 column (elucent 1 mM NaHCO$_3$) and conductivity detector. Oxygen consumption was measured with an oxygen-sensitive electrode (Wiss. Techn. Werkst., Weilheim). Pulse radiolysis experiments were carried out using a 2.8 MeV van-de-Graaff electron accelerator. The pulse duration was 1 $\mu$s and the absorbed doses were between 6 and 30 Gy. For the measurement of charged species an a.c. conductivity setup with a 40 V a.c. generator of 10 MHz frequency was used [26, 27].

**Conclusion**

The present system showed that OH addition to double bonds in the presence of oxygen creates radicals which in their subsequent reactions may result in the fragmentation of the carbon skeleton. This reaction is, however, very sensitive to substituents flanking the bond to be broken. There is a number of other competing reactions which at present make it difficult to predict the preference of a given route with some certainty.