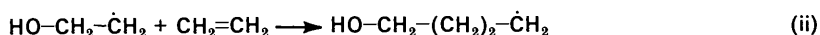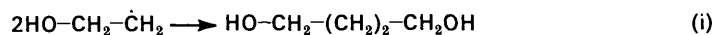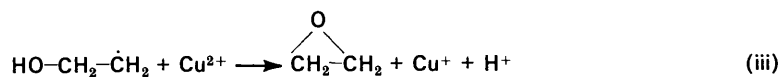# Hydroxyl Radical-induced Oligomerization of Ethylene in Deoxygenated Aqueous Solution

By **Turan Söylemez** and **Clemens von Sonntag**,* Institut für Strahlenchemie, im Max-Planck-Institut für Kohlenforschung, Stiftstrasse 34–36, D–4330 Mülheim a.d. Ruhr, West Germany
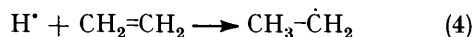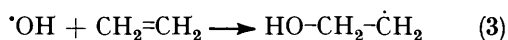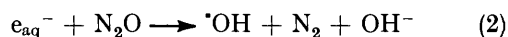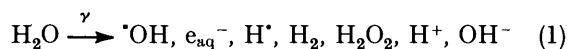
Deoxygenated aqueous solutions of ethylene (4×10^{-3}M) and nitrous oxide (9×10^{-3}M) were irradiated with γ-^{60}Co rays at dose rates of 2.6×10^{15} and 2.1×10^{16} eV $g^{-1} s^{-1}$. The most prominent among the 19 products determined are butane-1,4-diol, hexane-1,6-diol, and octane-1,8-diol. A satisfactory material balance with respect to primary water radicals was obtained. In the radiolysis of N_2O-containing water the major part (*ca.* 90%) of the primary radicals are OH radicals which are scavenged by ethylene to give β-hydroxyethyl radicals. These radicals either combine, butane-1,4-diol being the product [reaction (i)], or add to ethylene [reaction (ii)]. The

$$2HO-CH_2-\dot{C}H_2 \longrightarrow HO-CH_2-(CH_2)_2-CH_2OH \qquad \text{(i)}$$

$$HO-CH_2-\dot{C}H_2 + CH_2=CH_2 \longrightarrow HO-CH_2-(CH_2)_2-\dot{C}H_2 \qquad \text{(ii)}$$

self-termination rate constant has been measured by pulse radiolysis $[2k(i) = (5 \pm 2) \times 10^8 \text{ l mol}^{-1} \text{s}^{-1}]$. The propagation rate constant $[k(ii) = (3 \pm 2) \times 10^4 \text{ l mol}^{-1} \text{s}^{-1}]$ has been derived from the dose rate dependence of G(diols) by computer-aided fitting. The β-hydroxyethyl radicals are readily oxidized by copper(II) ions (5×10^{-3} M). The major product is ethylene oxide [reaction (iii)], and little (*ca.* 3%) ethylene glycol is formed [reaction (iv)].

$$HO-CH_2-\dot{C}H_2 + Cu^{2+} \longrightarrow \overset{O}{\overset{\diagup\diagdown}{CH_2-CH_2}} + Cu^+ + H^+ \qquad \text{(iii)}$$

$$HO-CH_2-\dot{C}H_2 + Cu^{2+} + H_2O \longrightarrow HO-CH_2-CH_2-OH + Cu^+ + H^+ \qquad \text{(iv)}$$

In free radical studies on unsaturated compounds in deoxygenated solutions often only the monomeric products are investigated. However, free radicals readily add to C=C double bonds, and at steady state concentrations of radicals there might already be appreciable oligomerization even at relatively low olefin concentrations. Such an oligomerization reaction can be most conveniently studied with the simplest olefin, ethylene, and a single radical source. The latter prerequisite is nearly ideally fulfilled by the radiolysis of N_2O-saturated water, as this system yields mainly OH radicals [G(OH) 5.4] and only some hydrogen atoms [G(H) 0.55] as primary radicals [reactions (1) and (2)].

$$H_2O \overset{\gamma}{\longrightarrow} \text{·}OH, e_{aq}^-, H\text{·}, H_2, H_2O_2, H^+, OH^- \qquad (1)$$

$$e_{aq}^- + N_2O \longrightarrow \text{·}OH + N_2 + OH^- \qquad (2)$$

$$\text{·}OH + CH_2=CH_2 \longrightarrow HO-CH_2-\dot{C}H_2 \qquad (3)$$

$$H\text{·} + CH_2=CH_2 \longrightarrow CH_3-\dot{C}H_2 \qquad (4)$$

The radiolysis of aqueous solutions of ethylene has already been investigated [1-6] prior to this study. It has been shown that OH radicals and H atoms are scavenged by ethylene (for rate constants see refs. 7 and 8) most likely by addition to the double bond [5,6] [reactions (3) and (4)]. In contradiction to this view, it has also been suggested [2] that OH radicals abstract to a considerable extent a hydrogen atom from ethylene to give vinyl radicals.

The ethylene-derived radicals add to ethylene forming high molecular weight material. This polymerization can be inhibited by copper(II) ions which readily oxidize the primary β-hydroxyethyl radicals [from reaction

(3)].[5,6] The latter reaction has also been studied using Fenton's reagent containing copper(II) ions.[9]

The data from the present product and pulse radiolysis study allow the conclusions drawn in earlier work [1-6,9] to be supplemented and to some extent corrected.

EXPERIMENTAL

Ethylene (Messer-Griesheim) and N_2O (Hoechst) which were found to contain <10 p.p.m. O_2 (as measured with Elcoflux C5) were used without any further purification except in pulse radiolysis studies where the N_2O was further freed from O_2 with the help of an Oxisorb column (Messer-Griesheim). In order to obtain the appropriate mixtures, the flow rates of ethylene and N_2O were controlled by flow meters (Shorate Brooks Instruments). The concentrations of ethylene and N_2O in the aqueous phase were calculated from the flow rates of these gases and their known solubilities in water.[10] Triply distilled water was saturated with the gas mixture for 30 min, the gas flow was stopped, and the samples were irradiated in a Nuclear Engineering Ltd. γ-^{60}Co source. Pulse radiolysis experiments were carried out with 1 μs electron pulses (0.2—2 krad) from a 3 MeV van de Graaff electron accelerator (High Voltage Engineering Corp.; type K). All experiments were carried out at room temperature.

G.l.c. analysis (Varian 1400 and Carlo Erba 2900) of some products was carried out by injecting the aqueous solutions directly into the columns (2 m, 2% P-4000 on Chromosorb WAW-DCMS, temperature-programmed over 120—210°, 6° min^{-1}, for butanol, hexanol, octanol, and the diols; 6 m, 10—15% P-4000 on Chromosorb WAW-DCMS, at 85° for acetaldehyde, ethylene oxide, ethanol, and butyraldehyde). To determine the lower hydrocarbons, the gas phase of the irradiated solutions was analysed [11] in a 140 m SF96 glass capillary column.

For g.l.c.–m.s. analyses dried samples were trimethyl-

silylated [12] and separated on a 72 m OV-101 glass capillary column, temperature programmed over 70—220°, 4° min^{-1}. A typical chromatogram is shown in Figure 1. Ethylene glycol was determined *via* formaldehyde after periodate oxidation.[13] Prior to this measurement, the solutions were
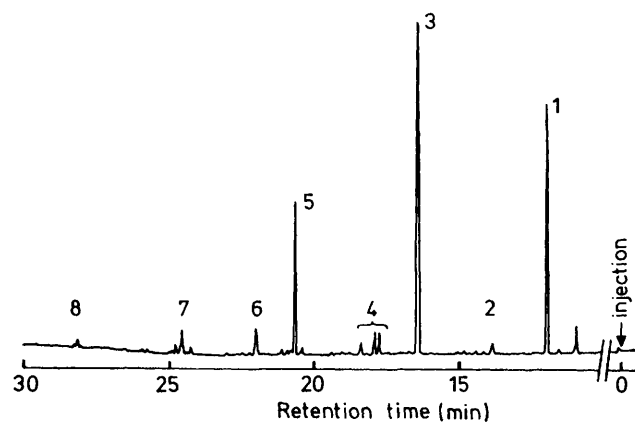

FIGURE 1 Gas chromatogram of the trimethylsilylated diols from a solution containing 9×10^{-3}M-N_2O and 4×10^{-3}M-ethylene irradiated for 60 min at the dose rate of 2.6×10^{15} eV g^{-1} s^{-1}: (1) butane-1,4-diol; (2) non-terminal hexanediols; (3) hexane-1,6-diol; (4) non-terminal octanediols; (5) octane-1,8-diol; (6) non-terminal decanediols; (7) decane-1,10-diol; (8) dodecane-1,12-diol

freed from ethylene oxide by a vigorous gas stream immediately after irradiation, and the copper ions which interfere with the assay were eliminated with an ion exchanger.

RESULTS

Product Analysis.—Solutions containing 4×10^{-3}M-ethylene and 9×10^{-3}M-N_2O were irradiated at dose rates of 2.1×10^{16} and 2.6×10^{15} eV g^{-1} s^{-1}. The product yields

Products and their G values in the γ-radiolysis of deoxygenated N_2O containing $(9 \times 10^{-3}$M) solutions of ethylene $(4 \times 10^{-3}$M) at two different dose rates

Product	Dose rate (eV g^{-1} s^{-1})	
	2.6×10^{15}	2.1×10^{16}
Acetaldehyde	0.48	0.40
Ethylene oxide	Absent	Absent
Ethanol	0.40	0.44
Ethylene glycol	Absent	Absent
But-1-ene	<0.01	Not measured
Butane	<0.02	Not measured
Butyraldehyde	0.07	Not measured
Butanol	0.21	Not measured
Hex-1-ene	Absent	Not measured
Hexane	<0.01	Not measured
Hexanol	0.06	Not measured
Octanol	0.07	Not measured
Butane-1,4-diol	0.32	1.10
Hexane-1,6-diol	0.68	0.70
Non-terminal hexanediols	0.04	0.05
Octane-1,8-diol	0.46	0.23
Non-terminal octanediols	0.10	0.08
Decane-1,10-diol	0.13	0.03
Non-terminal decanediols	0.06	0.04
Dodecane-1,12-diol	0.02	

increased linearly with dose in the dose range from 2.6×10^{17} to $2\,6 \times 10^{18}$ eV g^{-1} From the yield–dose plots G values were calculated which are given in the Table. G.l.c.–m.s. analysis revealed that the $\alpha\omega$-diols predominate, but

with increasing chain length the contribution of non-terminal diols considerably increases (*cf.* Figure 1).

Some experiments were done with solutions containing Cu^{2+} ions $(5 \times 10^{-3}$M). The formation of the diols observed in the absence of Cu^{2+} ions was suppressed but ethylene glycol was formed with a G value of 0.2. It was confirmed that the major product is ethylene oxide as reported earlier,[6] but it was not measured quantitatively.

Pulse Radiolysis.—Aqueous solutions containing 2×10^{-3}M-ethylene and 2×10^{-2}M-N_2O subjected to a 1 μs pulse of 3 MeV electrons show an absorption which gradually increases with the wavelength decreasing from 260 to 225 nm. The absorption is considered to be largely due to the β-hydroxyethyl radical [from reaction (3)] with a minor contribution of the ethyl radical [from reaction (4)]. Both radicals are expected to give a similar absorption.[3] Using G(total radicals) $= 6$ the molar extinction coefficients of the β-hydroxyethyl radical (the major contributor) were calculated, λ 225 (ϵ 1 450 l mol^{-1} cm^{-1}) 230(95), 240(450), 250(400), and 260(250) nm These extinction coefficients are considered to be accurate only to within 25%, especially at the lower wavelengths The extinction coefficient at 240 nm is in agreement with the reported [3] value of 400 ± 60 l mol^{-1} cm^{-1}. The absorption decays by second order. Using G(total radicals) 6 a rate constant of $(5 \pm 2) \times 10^8$ l mol^{-1} s^{-1} was calculated which is in agreement with the value of $(6.3 \pm 1) \times 10^8$ l mol^{-1} s^{-1} reported previously.[3]
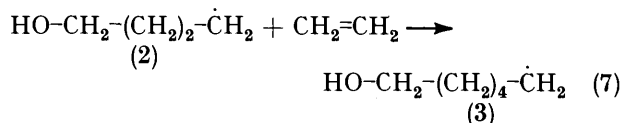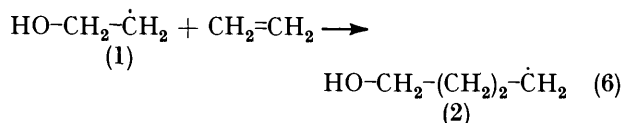
DISCUSSION

The data shown in the Table indicate that in the present study the measured products account for 80% of the primary radicals (OH and H) at the low dose rate and for *ca.* 90% at the high dose rate conditions despite the fact that not all identified products were measured under the latter conditions. Because of this reasonable material balance one can draw some conclusions on the reaction mechanism.

Oligomerization.—In previous studies [1,2,4] it was not possible to analyse for the diols. At the high ethylene concentrations used in other work [2] oligomerization proceeded to such an extent that only high molecular weight material was found, allegedly not containing any oxygenated groups. It was concluded [2] that a substantial proportion of OH radicals does not add to ethylene but abstracts a hydrogen atom to give vinyl radicals. The present data suggest (*cf.* high yield of diols, Table) that the major reaction of the OH radicals is the addition to the double bond [reaction (3)], and no product was observed which would strongly indicate (*e.g.* buta-1,3-diene) the presence of vinyl radicals in this system.

Figure 2 shows a schematic representation of the G values of the various diols at two different dose rates. At the higher dose rate (Figure 2a) the lowest possible diol (butane-1,4-diol) predominates and the yields of the higher ones steadily decrease. Under this condition termination by combination of two β-hydroxyethyl radicals [reaction (5)] is favoured over the polymerization reactions [*e.g.* reactions (6) and (7)].

$$2 \text{ HO-CH}_2\text{-CH}_2^{\cdot} \longrightarrow \text{HO-CH}_2\text{-(CH}_2)_2\text{-CH}_2\text{-OH} \quad (5)$$
$$(1)$$
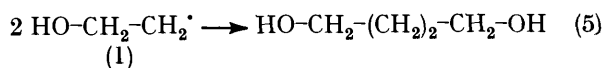
At the lower dose rate (Figure 2b) the oligomerization gains importance which results in a reduction of the butane-1,4-diol yield and an increase of the long-chain material. The diol showing the maximum yield is now hexane-1,6-diol [combination product of (1) and (2)].

$$HO-CH_2-\dot{C}H_2 + CH_2=CH_2 \longrightarrow$$
$$(1)$$

$$HO-CH_2-(CH_2)_2-\dot{C}H_2 \quad (6)$$
$$(2)$$

$$HO-CH_2-(CH_2)_2-\dot{C}H_2 + CH_2=CH_2 \longrightarrow$$
$$(2)$$

$$HO-CH_2-(CH_2)_4-\dot{C}H_2 \quad (7)$$
$$(3)$$

This behaviour can be simulated by computer calculations. There it has been assumed that the propagation rate of all radicals is equal ($e.g.$ $k_6 = k_7$) and that the termination rate constant of 5×10^8 l mol^{-1} s^{-1} as determined for the lowest member of this series holds for the somewhat higher ones. With these assumptions the trend of the data in Figure 2 can only be fitted if $k_6 = (3 \pm 2) \times 10^4$ l mol^{-1} s^{-1}.

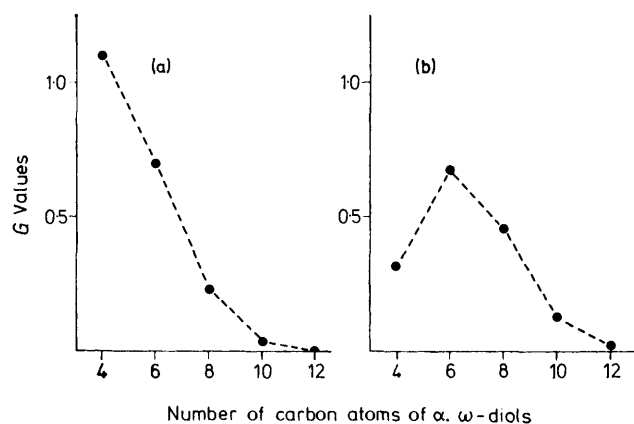There is a considerable controversy with respect to the rate constant of the propagation reactions [$e.g.$ reactions

Number of carbon atoms of α. ω-diols

FIGURE 2 Distribution of G(diols) at two different dose rates: (a) 2.1×10^{16} eV g^{-1} s^{-1}, (b) 2.6×10^{15} eV g^{-1} s^{-1}

(6) and (7)]. Values of 10^7 l mol^{-1} s^{-1} (ref. 2) and 2×10^6 (ref. 6) have been calculated. The former value has been deduced from a competition with oxygen, the latter from the kinetics of a rather complex system involving Cu^{2+} and [Cu$^+$-olefin]. We feel that the present value of $(3 \pm 2) \times 10^4$ l mol^{-1} s^{-1} is more reliable, because the present system using the yield data, the dose rate, and the bimolecular decay rate allows a straightforward determination of the rate constant.

Rearrangement of Radicals.—Among the products butyraldehyde and non-terminal diols are found. This observation might be rationalized by a rearrangement of radicals [$e.g.$ reaction (8)]. In reaction (8) an alkyl
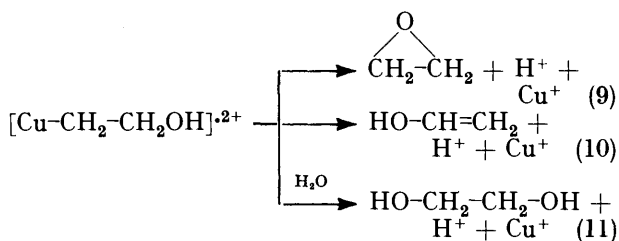
$$HO-CH_2-(CH_2)_2-\dot{C}H_2 \longrightarrow HO-\dot{C}H-(CH_2)_2-CH_3 \quad (8)$$
$$(2) \qquad\qquad\qquad (4)$$
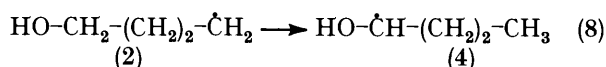
radical (2) is transformed into an α-hydroxyalkyl radical

(4). As an intermolecular process such a reaction is well established [14-16] the rate constants being $ca.$ 30 l mol^{-1} s^{-1}. Recently it has been shown [17] with n-alkane diols that such a process also occurs intramolecularly with an activation energy of only $ca.$ 29 kJ mol^{-1}. Therefore reaction (8) may well proceed and butyraldehyde (and part of the butanol) should be formed in the disproportionation reactions (see below) of radical (4). Nonterminal diols are observed whose structures have not been unequivocally assigned but the mass spectra of the trimethylsilylated material do not contradict the assumption that rearranged radicals such as (4) also propagate by adding ethylene.

Termination.—Straight-chain alkyl radicals like the ethyl radical have a high tendency to combine. Their disproportionation to combination ratio (k_d/k_c) is $ca.$ 0.18.[18] For the α-hydroxyethyl radical a value of $k_d/k_c = 0.43$ has been reported.[19] Besides the β-hydroxyethyl radicals (1) and ethyl radicals there are also the long-chain hydroxyalkyl radicals like (2) and (3) and the rearranged radicals like (4). Assuming that the long-chain hydroxyalkyl radicals [(2), (3), $etc.$] behave similarly to the ethyl radicals they would predominantly combine. This is in agreement with the fact that no but-1-en-4-ol was detected ($G < 0.02$). The rearranged radical (4) will have the same properties as the α-hydroxyethyl radical and will show considerable disproportionation. Hence the relatively high yield of butyraldehyde is well understood. Assuming a similar k_d/k_c for the β-hydroxyethyl radicals as is reported for the α-hydroxyethyl radicals [they are both expected to give the same products, ethanol and vinyl alcohol, the latter rearranging into acetaldehyde ($cf.$ ref. 20)]; G(acetaldehyde) and G(ethanol) are of the expected magnitude.

It has been shown [5,6,9] that the β-hydroxyethyl radicals are readily oxidized by Cu^{2+}. In the case of the radical derived from t-butyl alcohol, $^{\bullet}$CH$_2$C(CH$_3$)$_2$OH, if generated at low pH with Fenton's reagent in the presence of Cu^{2+}, isobutylene glycol is the major product,[9] whereas at neutral pH the β-hydroxyethyl radical is reported [5,6] to give exclusively ethylene oxide. In principle two reactive intermediates have been considered, a copper–radical complex [Cu-CH$_2$-CH$_2$-OH]$^{\bullet 2+}$, or the carbonium ion, HO-CH$_2$-CH$_2^+$. These reactive

$$[Cu-CH_2-CH_2OH]^{\bullet 2+} \longrightarrow$$
$$\overset{O}{\overset{/\backslash}{CH_2-CH_2}} + H^+ + Cu^+ \quad (9)$$
$$\longrightarrow HO-CH=CH_2 + H^+ + Cu^+ \quad (10)$$
$$\overset{H_2O}{\longrightarrow} HO-CH_2-CH_2-OH + H^+ + Cu^+ \quad (11)$$

intermediates could undergo three reactions [$e.g.$ reactions (9)—(11)]. In refs. 5 and 6 reaction (9) was suggested to be the sole process whereas in ref. 9 reaction (11) has been considered.

Under the experimental conditions of ref. 6 it is

difficult if not impossible to distinguish between the two isomers, namely ethylene oxide [from reaction (9)] and acetaldehyde [from reaction (10), vinyl alcohol being the precursor]. Under our experimental conditions ethylene oxide and acetaldehyde are well separated, and it was confirmed that in the presence of Cu^{2+} only ethylene oxide is formed and acetaldehyde which is formed in the absence of Cu^{2+} (see Table) is no longer produced. The third conceivable product, ethylene glycol [from reaction (11)], has to be considered not only because of the results given in ref. 9 but also because the oxidation of the α-ethoxyethyl radical with $Fe(CN)_6^{3-}$ leads to the hemiacetal of acetaldehyde and ethanol, the possible deprotonation product ethyl vinyl ether not being observed.[21] In fact, our results show that in the presence of Cu^{2+} ethylene glycol is formed with a G value of 0.2. This means that reaction (11) plays only a minor role.

The apparent discrepancy between the Fenton's reagent study [9] and the radiolytic studies (refs. 5 and 6 and the present work) might also be reconciled. It is quite possible that also in the Fenton's reagent system the major primary product is the epoxide. However, under these strongly acidic conditions (pH 0.8) the epoxide is hydrolysed to the glycol very quickly (half life [22] of isobutylene oxide <2 s).

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