Chain Formation of Acetaldehyde in the γ-Radiolysis of Deaerated Ethylene Glycol

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Summary High yields (G ⩽ 200,000), of acetaldehyde were found during an investigation of the γ-radiolysis of pure, deaerated ethylene glycol.

DURING the γ-radiolysis of pure ethylene glycol at low dose, 2-methyl-1,3-dioxolan was formed in high yields. This compound had also been observed at a dose of $2 \cdot 6 \times 10^{21}$ eV g^{-1}, by Barker et al.[2] who suggested that its formation took place through a vinyl alcohol or ethylene oxide intermediate, resulting from the dissociation of the parent ion.

The formation of 2-methyl-1,3-dioxolan was also found to occur[2] in a condensation reaction between acetaldehyde, which is formed as a primary product, and ethylene glycol. The high yield of 2-methyl-1,3-dioxolan must therefore be related to the yield of acetaldehyde.

We now report evidence for the existence of a chain mechanism leading to the formation of acetaldehyde with G-values up to 200,000 at room temperature.

Ethylene glycol (Merck "pro-analysi") was used without further purification as no difference in the acetaldehyde yield between this alcohol and ethylene glycol purified by fractionation on a spinning band column was found. Irradiations were carried out in a gamma-beam 650 (AECL) delivering dose-rates between 10^{15} eV g^{-1} min^{-1} and 5×10^{18} eV g^{-1} min^{-1} depending on the sample–source distance. For the dose-rate study the samples received a dose of 10^{18} eV g^{-1}. For the dose study the dose-rate was $4 \cdot 1 \times 10^{16}$ eV g^{-1} min^{-1}.

The samples were analysed by gas chromatography on a Varian 1200 gas chromatograph with a flame ionisation detector using a 6 ft × ⅛ inch glass column packed with 10% Carbowax 1540 on Chromosorb WAW at 60 °C.

As the reaction between acetaldehyde and ethylene glycol was very rapid[2] it was not possible to measure the initial acetaldehyde concentration directly. The relationship between the initial acetaldehyde concentration and the equilibrium 2-methyl-1,3-dioxolan concentration was determined by converting the 2-methyl-1,3-dioxolan concentration, as measured gas chromatographically, into acetaldehyde concentration.

To correlate our results with those of Barker et al.[1] the
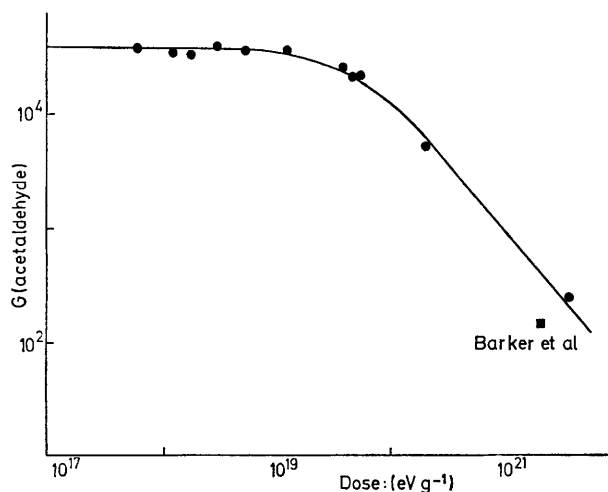

FIGURE 1

effect of dose on the yield of the products was studied (Figure 1). Considering the difference in experimental

conditions *e.g.* dose-rate, the true G(acetaldehyde) obtained by Barker *et al.*, as calculated from their 2-methyl-1,3-dioxolan yield, is in reasonable agreement with the results of the present study. This indicates that the high yields of acetaldehyde observed at low doses of the present study are essentially correct.

These extraordinarily high yields suggest the existence of a chain reaction responsible for the formation of acetaldehyde. To obtain information concerning the nature of this reaction we studied the effect of dose-rate.

The existence of a classical bi-radical terminated chain reaction is demonstrated by Figure 2. The rate of change
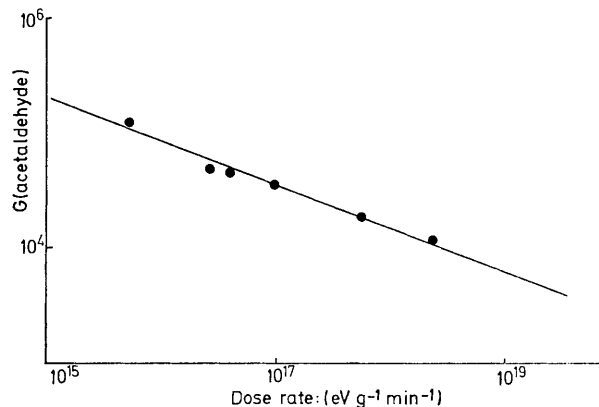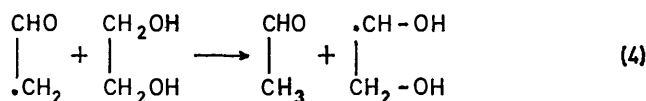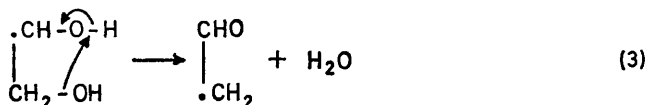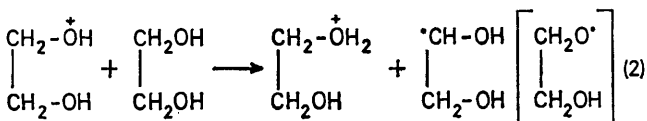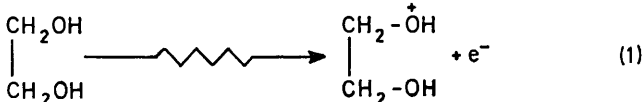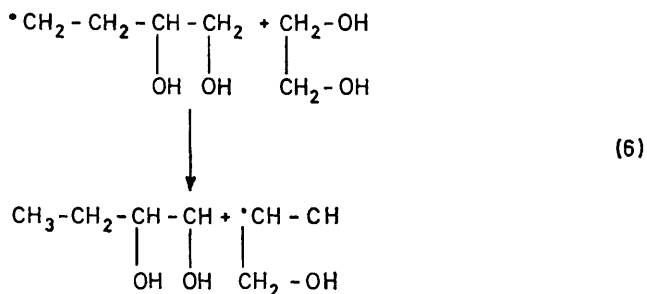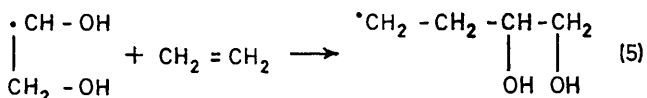

FIGURE 2

of log (yield) with log (dose-rate) equals -0.48 which is very close to the theoretically expected value of -0.5.

$$\begin{matrix} CH_2OH \\ | \\ CH_2OH \end{matrix} \longrightarrow \begin{matrix} CH_2\text{-}\overset{+}{O}H \\ | \\ CH_2\text{-}OH \end{matrix} + e^- \qquad (1)$$

$$\begin{matrix} CH_2\text{-}\overset{+}{O}H \\ | \\ CH_2\text{-}OH \end{matrix} + \begin{matrix} CH_2OH \\ | \\ CH_2OH \end{matrix} \longrightarrow \begin{matrix} CH_2\text{-}\overset{+}{O}H_2 \\ | \\ CH_2OH \end{matrix} + \begin{matrix} {}^{\bullet}CH\text{-}OH \\ | \\ CH_2\text{-}OH \end{matrix} \left[\begin{matrix} CH_2O^{\bullet} \\ | \\ CH_2OH \end{matrix} \right] \quad (2)$$

$$\begin{matrix} {}^{\bullet}CH\text{-}O\text{-}H \\ | \\ CH_2\text{-}OH \end{matrix} \longrightarrow \begin{matrix} CHO \\ | \\ {}^{\bullet}CH_2 \end{matrix} + H_2O \qquad (3)$$

$$\begin{matrix} CHO \\ | \\ {}^{\bullet}CH_2 \end{matrix} + \begin{matrix} CH_2OH \\ | \\ CH_2OH \end{matrix} \longrightarrow \begin{matrix} CHO \\ | \\ CH_3 \end{matrix} + \begin{matrix} {}^{\bullet}CH\text{-}OH \\ | \\ CH_2\text{-}OH \end{matrix} \qquad (4)$$

Reactions (3) and (4) cause the chain reaction leading to the formation of acetaldehyde.

On the basis of their e.s.r. experiments, Bazhin *et al.*[3] suggested that 1,2-dihydroxyethyl radicals eliminated water. This was confirmed by Seidler and von Sonntag[4] who also suggested that these radicals are the precursors of acetaldehyde in N_2O-saturated aqueous solutions of ethylene glycol.

To prove that the primary source of acetaldehyde in pure ethylene glycol is the 1,2-dihydroxyethyl radical we studied the effect of ethylene as radical scavenger. The only telomerisation product found in ethylene-saturated

$$\begin{matrix} {}^{\bullet}CH\text{-}OH \\ | \\ CH_2\text{-}OH \end{matrix} + CH_2 = CH_2 \longrightarrow \begin{matrix} {}^{\bullet}CH_2\text{-}CH_2\text{-}CH\text{-}CH_2 \\ | \quad | \\ OH \quad OH \end{matrix} \quad (5)$$

$$\begin{matrix} {}^{\bullet}CH_2\text{-}CH_2\text{-}CH\text{-}CH_2 \\ | \quad | \\ OH \quad OH \end{matrix} + \begin{matrix} CH_2\text{-}OH \\ | \\ CH_2\text{-}OH \end{matrix}$$
$$\downarrow$$
$$\begin{matrix} CH_3\text{-}CH_2\text{-}CH\text{-}CH \\ | \quad | \\ OH \quad OH \end{matrix} + \begin{matrix} {}^{\bullet}CH\text{-}CH \\ | \\ CH_2\text{-}OH \end{matrix} \qquad (6)$$

ethylene glycol was butane-1,2-diol. This can be ascribed to reactions (5) and (6).

These results are evidence for the existence of a chain reaction leading to acetaldehyde formation and a definite indication that the 1,2-dihydroxyethyl radical is involved in this reaction. If the mechanism suggested is correct the reaction could be of interest as an industrial synthetic method.

[1] S. A. Barker, J. S. Brimacombe, and E. D. M. Eades, *Radiation Res.*, 1964, **22**, 357.
[2] P. J. Venter, H. J. van der Linde, and R. A. Basson, to be published.
[3] N. M. Bazhin, E. V. Kuznetzov, N. N. Baednov, and V. Voevodskii, *Kinetike i Kataliz*, 1966, **7**, 732.
[4] F. Seidler and C. von Sonntag, *Z. Naturforsch.*, 1969, **246**, 780.