# Products of Low Molecular Weight in the Radiolysis of Aqueous Solutions of Ethylene

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IT has been shown that a "polymer" is the major product in the radiolysis of dilute aqueous solutions of ethylene[1] together with small amount of aldehydes and hydrogen peroxide.[1,2] It is also known that the yield of this "polymer" is directly proportional to the initial ethylene concentration[1] and that the polymeric product does not contain OH groups.[1,3]

These results suggest that other unidentified products may be formed. In particular oxygenated products should exist to account for the OH radicals produced in the water radiolysis unless the greater part of these radicals disappear in the abstraction reaction

$$OH + C_2H_4 \rightarrow H_2O + C_2H_3 \qquad (1)$$
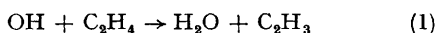
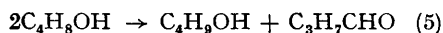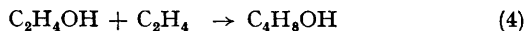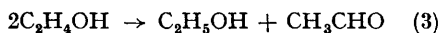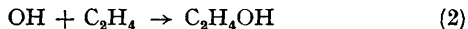However, this reaction is said to be energetically unfavourable[4] and consequently considerable doubt exists as to the nature of the primary reaction. We have completed a more thorough analysis of product distribution in an attempt to clarify the initial stages in the radiolysis.

Gas-chromatographic analysis of the reaction products, when ethylene solutions ($1-4 \times 10^{-3}$M) are irradiated to total doses between 10^{18} and 2×10^{19} ev/ml., revealed the presence of butane, hexane, octane, decane, acetaldehyde, n-butyraldehyde, ethanol, butanol, and traces of hydrogen peroxide and propanol. The yields of these products are strongly dependent on dose, tending to decrease with increasing dose, and on the ethylene concentration, tending to increase with increasing [C_2H_4]. Preliminary indications are that the G-values of products, at a dose of 8×10^{17}

ev/ml., increase up to $[C_2H_4] = 3 \times 10^{-4}$M and then remain constant.

As an indication of the magnitude of product yields G-values from a typical experiment are given in the Table.

The appreciable amounts of ethanol and butanol suggest that OH radicals add to ethylene rather than abstract from it.

$$OH + C_2H_4 \rightarrow C_2H_4OH \qquad (2)$$

$$2C_2H_4OH \rightarrow C_2H_5OH + CH_3CHO \qquad (3)$$

$$C_2H_4OH + C_2H_4 \rightarrow C_4H_8OH \qquad (4)$$

$$2C_4H_8OH \rightarrow C_4H_9OH + C_3H_7CHO \qquad (5)$$

The stoicheiometry requires that equal amounts of ethanol and acetaldehyde, and similarly of butanol and butyraldehyde, be formed. That the experimental aldehyde yields are lower than the corresponding alcohol yields is probably due to the competition between ethylene and aldehyde (but not alcohol) for solvated electrons. Absolute rate constants for these reactions support this suggestion: $k(e_{aq}^- + CH_3CHO) = 3.5 \times 10^9$M^{-1} sec.$^{-1,5}$ $k(e_{aq}^- + C_2H_4) < 2.5 \times 10^6$M^{-1} sec.$^{-1,1}$ and $k(e_{aq}^- + C_2H_5OH) < 1 \times 10^5$M^{-1} sec.$^{-1,6}$

If we thus take the alcohol yields as the initial yields of reaction (3) and (5), we find that

$G(2) = 2[G(C_2H_5OH) + G(C_4H_9OH)] = 1.7$. Consequently $k_1/k_2 = 0.3$ which is in contradiction to the value of 2 derived by Cullis *et al.*,[1] but is in agreement with expectations based on energetic considerations.[4] It is also in reasonable agreement with the value of 0.17 derived from a study of the radiolytic oxidation of ethylene in aqueous solution.[7]

TABLE

$G(products)$ *in the radiolysis of a* 4×10^{-3}M *aqueous solution of ethylene at a dose of* 8×10^{17} *ev/ml. in neutral solution*

Product				G-value
Butane	..	..	..	..	0.90
Hexane	..	..	..	..	0.35
Octane	..	..	..	..	0.07
Decane	..	..	..	..	0.15
Acetaldehyde	..	..	..	0.15
Butyraldehyde	..	..	..	0.12
Ethanol	..	..	..	..	0.30
Butanol	..	..	..	..	0.54
Propanol	..	..	..	..	~0.05
H_2O_2 ..	..	..	..	..	0.09

The high yields of butane and hexane suggest that chain termination occurs rapidly under these conditions as might be expected from polymerization kinetics.

(*Revised, February 20th*, 1967; *Com.* 164.)

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