Effect of Acid on the Radiolysis of Ethanol

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THE increase in $G(H_2)$ from 4·9—5·6 with increasing acid concentration in the radiolysis of ethanol was interpreted by Adams and Sedgwick[1] as the scavenging of solvated electrons in the spurs.

We have determined the yields of H_2, $CH_3 \cdot CHO$, and butanediol as a function of acid concentration and have obtained results which do not agree with the predictions of their mechanism. Recently Freeman has published additional data[2] on the acid effect and concluded that his results are also incompatible with the Adams–Sedgwick mechanism. Considerable uncertainty, thus, exists on this effect, which is fundamental to the understanding of the radiolysis mechanism. We now offer an explanation for the experimental differences by suggesting a new mechanism.

The methods employed in the purification of samples, irradiations,[3] and hydrogen analyses, have been previously described. Due to the acid catalysed formation of acetal, acetaldehyde was determined by a modification of the dinitrophenylhydrazine method.[4] Butanediol was determined by gas chromatography[2,3] with a 5 ft. × $\frac{1}{8}$ in. stainless steel column packed with 1% FFAP on glass beads (60/80 mesh). It was necessary to concentrate these samples by a factor of 10 before analysis.

The effect of acid on product yields is shown in the Figure. Between 10^{-4}M- and 10^{-2}M-H_2SO_4, the yields of all three products increase with $\Delta G(H_2) = 0·65$, $\Delta G(CH_3 \cdot CHO) = 0·40$, and ΔG-(glycol) $= 0·35$. Above 10^{-2}M-H_2SO_4 no further increase is observed.

The increase in G(glycol) is in apparent contradiction to the results of Adams and Sedgwick.[1] In earlier experiments we found that G(glycol) *decreased* with increasing acid concentrations, due to a reaction in the inlet system of the gas chromatograph, which was eliminated by neutralisation of the acid before sample injection. This treatment gave results in agreement with Adams

and Sedgwick. Further work showed, however, that standard samples, neutralised before injection, still gave evidence of thermal reaction prior to analysis. The magnitude of this reaction was established under conditions comparable to the irradiated samples, and the glycol yields accordingly corrected as shown in the Figure. It is thus suggested that the discrepancy between the two sets of data is due to this effect and that the present results represent the true situation.
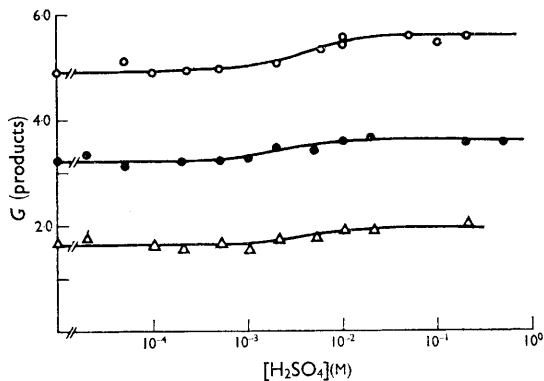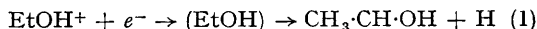

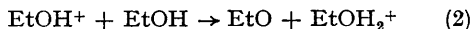FIGURE. *Product yield as a function of* [H_2SO_4] ○ Hydrogen, ● Acetaldehyde, △ Butane-2,3-diol.

The present data are not compatible with the predictions of the mechanism put forward by Adams and Sedgwick who suggest that the effect is due to scavenging of a back reaction (1).

$$EtOH^+ + e^- \rightarrow (EtOH) \rightarrow CH_3 \cdot CH \cdot OH + H \quad (1)$$

The net result is an increase of one molecule of hydrogen and one of acetaldehyde for each electron scavenged, the glycol yield remaining constant. In view of additional data the mechanism should be reformulated. In the first place, the parent
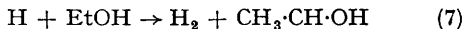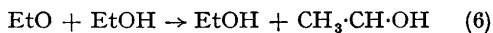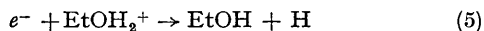
positive ion will not be involved in the neutralisation step in view of the rapidity of the ion–molecule reaction (2).[2,3,5]

$$2CH_3 \cdot CH \cdot OH \rightarrow CH_3 \cdot CHO + EtOH \quad (8)$$

$$2CH_3 \cdot CH \cdot OH \rightarrow (CH_3 \cdot CH \cdot OH)_2 \quad (9)$$

$$EtOH^+ + EtOH \rightarrow EtO + EtOH_2^+ \quad (2)$$

Neutralisation of the ethyl hydronium ion is not a back reaction and, by analogy with water, we may formulate (3) as a reaction in the spurs which leads to the reformation of ethanol.

$$EtO(CH_3 \cdot CH \cdot OH) + e^-_{solv} \rightarrow EtO^- \quad (3)$$

$$EtOH_2^+ + EtO^- \rightarrow 2EtOH \quad (4)$$
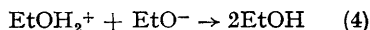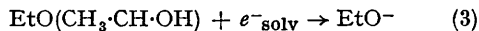
The influence of added acid is to scavenge reaction (3) and by so doing to produce an additional yield of hydrogen atoms via reaction (5). For each solvated electron scavenged, 2 additional hydroxyethyl radicals are produced in reactions (6) and (7).

$$e^- + EtOH_2^+ \rightarrow EtOH + H \quad (5)$$

$$EtO + EtOH \rightarrow EtOH + CH_3 \cdot CH \cdot OH \quad (6)$$

$$H + EtOH \rightarrow H_2 + CH_3 \cdot CH \cdot OH \quad (7)$$

We have recently shown that 1-hydroxyethyl radicals undergo both disproportionation and dimerisation and that the two processes are approximately equally important.[6] (Adams and Sedgwick considered dimerisation only.)
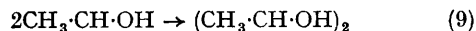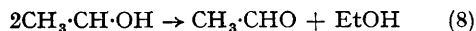
Taking $k_8 = k_9$ the mechanism predicts that $\Delta G(\text{glycol}) = \Delta G(CH_3 \cdot CHO) = 0\cdot5 \Delta G(H_2)$. The present results are in satisfactory agreement with this. Much better agreement would be obtained for $\Delta G(H_2) = 0\cdot75$ to $0\cdot8$ as obtained by other workers[2,7] and for this reason we believe that our $\Delta G(H_2)$ may be slightly low.

Our interpretation is, however, not compatible with the recent results of Russel and Freeman,[2] who conclude that the species scavenged by acid does not react with N_2O. We would expect N_2O to interfere with reaction (6) by competition for solvated electrons, as occurs in the bulk medium. Such an effect has been observed in the radiolysis of propan-2-ol,[8] which result also appears to be contradictory to Freeman's suggestion. The reasons for these differences are not immediately apparent.

The present interpretation is compatible with the results of Hayon and Moreau[7] and of Sherman[8] who, however, consider reaction (1) to be the back reaction. For the reasons given above we prefer the present explanation.

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[3] R. A. Basson and H. J. van der Linde, J. Chem. Soc. (A), 1967, 28.
[4] G. R. A. Johnson and G. Scholes, Analyst, 1954, 79, 217.
[5] J. J. J. Myron and G. R. Freeman, Canad. J. Chem., 1965, 43, 381.
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[7] E. Hayon and M. Moreau, J. Phys. Chem., 1965, 69, 4053.
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