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ALTERNATIVE ROUTES FOR THE FORMATION OF 2-METHYL-1,3-DIOXOLANE FROM ETHYLENE GLYCOL

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Abstract—The formation of 2-methyl-1,3-dioxolane can be brought about either by the γ-radiolysis of ethylene glycol or by the addition of concentrated acids to this compound.

INTRODUCTION

An unexpected but very interesting feature of the γ-radiolysis of ethylene glycol is the high yield of the product 2-methyl-1,3-dioxolane. Barker *et al.*[1] suggested that the formation of this product takes place through a vinyl alcohol or ethylene oxide intermediate. Such a mechanism, however, is difficult to visualize and seems rather unlikely. It was furthermore found[2] that acetaldehyde is formed as a primary product in a chain reaction during the γ-radiolysis of ethylene glycol. As acetic acid is also found as one of the products it seems logical to suggest that the dioxolane found during the γ-radiolysis of ethylene glycol is the result of the condensation reaction between the primary product, acetaldehyde, and ethylene glycol. If this is the case a complication arises as the exact yield of dioxolane in the γ-radiolysis of ethylene glycol cannot be measured directly. Consequently, the reaction between acetaldehyde and ethylene glycol was studied in some detail.

EXPERIMENTAL

Ethylene glycol (Merck "pro analysi") was purified on a 70-plate fractionating column, retaining only middle fractions. Analytical grade acetaldehyde was obtained from Riedel de Haën and the 2-methyl-1,3-dioxolane was supplied by Eastman Kodak Co. The study of the acid-catalyzed reaction was carried out in small test tubes fitted with rubber septums and maintained at a constant temperature in a water bath. The reagents were introduced into the system using a precision syringe.

All product analyses were done by gas chromatography on a Varian 1200 gas chromatograph equipped with a flame-ionization detector. A 2m × 0·25cm glass column packed with 10% carbowax 1540 on chromosorb WAW at 60°C was used for the analyses of acetaldehyde and 2-methyl-1,3-dioxolane.

RESULTS AND DISCUSSION

In the study of the γ-radiolysis of pure, deaerated ethylene glycol,[2] it was found that the formation of acetaldehyde takes place as a result of the decomposition of the 1,2-dihydroxy ethyl radical to yield water and the precursor (formyl methyl radical) of acetaldehyde. This means that the radiation-induced dehydration of ethylene glycol takes place via a radical mechanism.

To prove that the 2-methyl-1,3-dioxolane found in the γ-radiolysis of ethylene glycol is formed through the reaction of acetaldehyde with ethylene glycol, this reaction was studied in the presence of 2M H_2SO_4. It was found that a linear relationship exists between the initial acetaldehyde concentration and the equilibrium 2-methyl-1,3-dioxolane concentration. This relationship was also found to be valid for a concentration of acetic acid equivalent to that formed as a product in the γ-radiolysis of ethylene glycol with a G-value of 7·5.[1] The relationship which is in essence a calibration curve, enables one to convert the equilibrium dioxolane concentration in the system to the initial acetaldehyde concentration present before any reaction took place.

It was found that, in the absence of acid, the acetaldehyde disappeared, most probably due to the formation of the hemi-acetal, but almost no dioxolane appeared up to two hours after mixing. When acid was added, however, the dioxolane appeared instantaneously. The equilibrium state was reached within half a minute after mixing of the reactants. However, for uniformity, all analyses were carried out after 30 min.

In order to determine whether the relationship $[[C_4H_8O_2][[H_2O]/[(CH_2OH)_2][CH_3CHO]$ is constant for different acid concentrations, the effect of acid concentration on this equilibrium was studied. Fig 1 shows that for acid concentrations between 10^{-4} M and 2×10^{-1} M the relationship between the initial acetaldehyde concentration and the equilibrium dioxolane concentration is constant. In this concentration range the acid acts only as a catalyst for the condensation reaction between acetaldehyde and ethylene glycol. At acid concentrations higher than 2×10^{-1} M, however, a sharp increase in the equilibrium dioxolane concentration takes place, indicating the occurrence of a secondary reaction which also leads to dioxolane formation. Two possibilities exist, *viz.*:

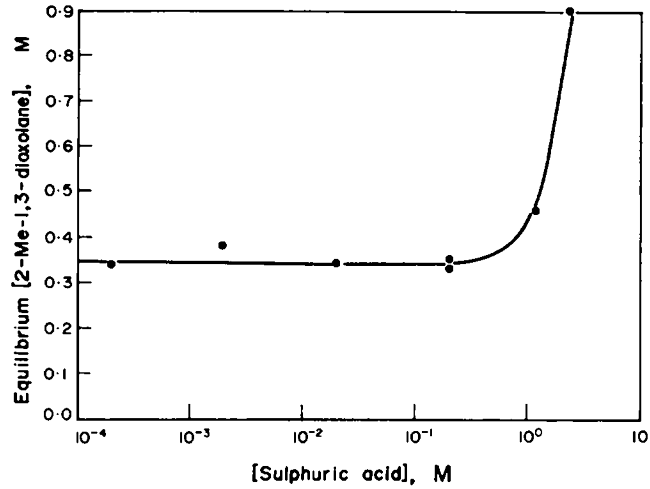
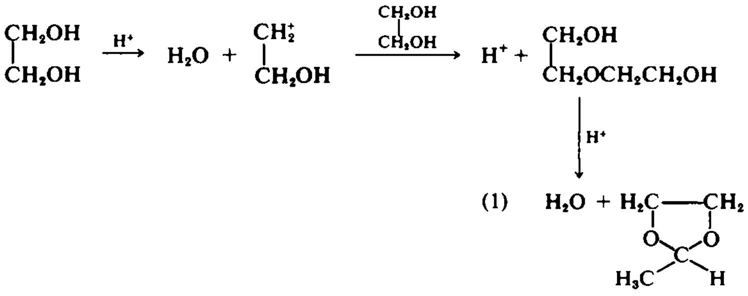
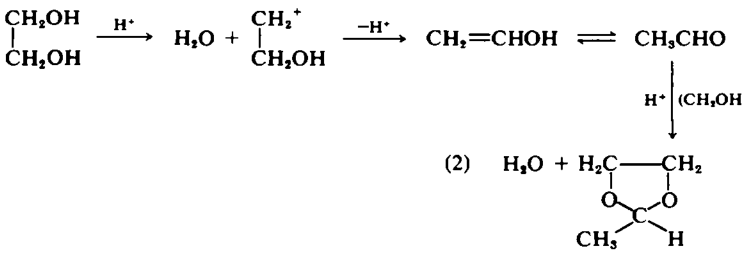


Fig 1. Effect of acid on equilibrium [2-Me-1,3-dioxolane]

(1) the direct formation of dioxolane out of ethylene glycol and sulphuric acid:



(2) the dehydration of ethylene glycol by sulphuric acid at concentrations higher than 2 × 10⁻¹ M to acetaldehyde which in turn reacts with ethylene glycol to yield the dioxolane:



Reaction (2) was experimentally verified. When 1 M sulphuric acid is added to pure ethylene glycol, large amounts of acetaldehyde, and hence dioxolane, are observed. When 1 M acetic acid is added, the same reactions occur but to a somewhat lesser extent. As they did not fall within the scope of the present study, these reactions were not investigated in greater detail. However, two important conclusions can be drawn from the results obtained:

(i) The formation of 2-methyl-1,3-dioxolane can be brought about either by the γ-radiation of ethylene glycol[2] where acetaldehyde is formed, in the absence of acid, as a primary product which further reacts with the ethylene glycol in the presence of the radiolytically produced acetic acid, or it can be accomplished by adding sulphuric acid (or, for that matter, acetic acid) to ethylene glycol in concentrations higher than 2×10^{-1} M.

(ii) The acetaldehyde observed in the γ-radiolysis and all other dehydration studies of ethylene glycol in the presence of even trace amounts of acid is merely that which remains in the system after equilibrium is reached, in as much as the conversion to dioxolane takes place almost instantaneously. Therefore, the initial yield of acetaldehyde can only be determined from the equilibrium concentration of 2-methyl-1,3-dioxolane. To achieve this, the concentration of acid present in the system must be taken into account.

REFERENCES

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