

The Radiation-Induced Rearrangement
of Glycols in Aqueous Solution

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by

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Abstract

The radiation-induced rearrangement and oxidation of ethylene glycol in deaerated aqueous hydrogen peroxide solution have been investigated. Ethylene glycol rearranges to form acetaldehyde in a chain reaction which is independent of the oxidative chain whereby ethylene glycol is oxidized to glycolic acid.

A mechanism has been proposed which is based on the rearrangement of the ethylene glycol radical, $\dot{\text{C}}\text{HOHCH}_2\text{OH}$, to the acetaldehyde precursor, $\dot{\text{C}}\text{H}_2\text{CHO}$, and also on the radical conversion reaction

$$\dot{\text{C}}\text{H}_2\text{CHO} + \text{CH}_2\text{OHCH}_2\text{OH} \longrightarrow \text{CH}_3\text{CHO} + \dot{\text{C}}\text{HOHCH}_2\text{OH}$$

which produces acetaldehyde and reforms $\dot{\text{C}}\text{HOHCH}_2\text{OH}$ thus providing the chain propagating step.

Acetaldehyde yields were also determined for systems containing either perchloric acid or nitrous oxide as the electron scavenger in place of the peroxide and the mechanism was found to be capable of explaining the results.

Other reactions which have been examined include the inhibition of the rearrangement by oxygen, the initiation of the rearrangement by UV radiation, and the rearrangement of other glycols-butane 2,3 diol and propylene glycol.

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1. Introduction

A. Radiation Chemistry

Radiation chemistry deals with the chemical changes initiated on the absorption of high energy radiation by a system. The radiation involved may be of an electromagnetic nature, such as x-rays or γ -rays, or of a corpuscular nature, such as α -particles, β -particles, protons, neutrons, or fission fragments. The radiation chemist studies the interactions between the radiation and the absorber, the formation and nature of the reactive intermediates produced when radiation is absorbed, and the subsequent reactions of these intermediates. Discussions of the interactions of various types of ionizing radiation with matter are found in Spinks and Woods (1), Allen (2), Swallow (3), and Vereshchinskii and Pikaev (4). Since the present work is limited to a consideration of reactions initiated by γ -rays from a Co^{60} source only the interaction of γ -rays with matter will be described here.

Energy is transferred from a photon to an absorber by three processes. Photoelectric absorption is the most important process for photons with energies up to several kiloelectron volts and for

materials of high atomic number. In this process an incident photon is completely absorbed by an electron of an atom of the absorber. The electron is released from the atom with a kinetic energy $E = h\nu - E_0$ where $h\nu$ is the energy of the incident photon and E_0 is the binding energy of the ejected electron.

The second process, Compton scattering, becomes the most prominent at energies above a few kiloelectron volts. It involves a collision between the photon and a bound electron resulting in the ejection of the electron and an inelastic scattering of the photon. If the scattered photon's energy is $h\nu'$ the energy of the electron is given by $E = h\nu - h\nu'$. The scattered photon may interact further with the absorbing material or it may escape from the system.

Pair production, the third mode of interaction, can occur only if the photon energy exceeds 1.02 MeV but is of no consequence for Co^{60} γ -rays which have energies of 1.173 and 1.332 MeV, only just above this threshold. In this process a photon is annihilated when passing very close to a heavy nucleus and an electron-positron pair is

created. The 1.02 MeV is required for the rest mass mc^2 of each particle and any remaining energy is converted into the kinetic energy of the electron and positron.

Above 0.1 MeV Compton scattering accounts for almost all the radiation absorption. This process results in the presence of high energy electrons within the system. These fast electrons interact with the molecules in the absorber and either eject electrons from the molecules to produce positive ions or excite the molecules to higher energy levels. Since the energy required to bring about these changes is only a few electron volts per molecule the fast electrons may affect several thousand molecules each.

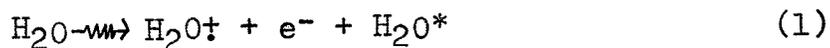
Secondary ejected electrons may have sufficient energy to continue this process. Other of these electrons with lower energies but still in excess of 100 eV form a branch or delta ray on the primary track as they lose their energy. The remaining energy transfer, which accounts for about half of the total, is by electrons with less than 100 eV energy. These interactions occur very near the original ionization site and the resulting

small volume elements where the energy is dissipated are called spurs (5,6). The rate of energy loss by a charged particle, known as the Linear Energy Transfer (LET), increases with decreasing particle velocity.

The ultimate result of all the energy transfer processes is the formation of many widely separated spurs of small radius, containing several ion pairs and excited molecules, together with isolated near-thermal electrons, within about 10^{-16} seconds of the passing of the photon. It is the subsequent reactions of these species which are of interest in radiation chemistry.

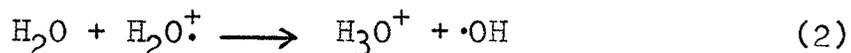
1.1 γ -Radiolysis of Aqueous Systems

Compton scattering is a non-specific mode of energy loss with the result that most of the energy is absorbed initially by the bulk solvent, water. The products formed initially in the spurs are ionized water molecules (H_2O^+), electrons (e^-) with energies in excess of thermal energy, and excited water molecules (H_2O^*).

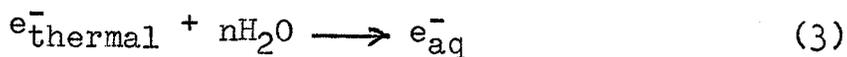


The H_2O^+ ion has an extremely short lifetime, of

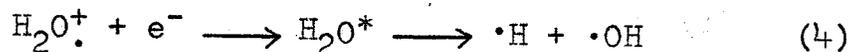
about 10^{-14} seconds, during which it reacts with a water molecule according to reaction (2).



The electrons are thermalized by means of collisions with water molecules and are stabilized as they orientate the surrounding water molecules through polarization (7).



Some of the electrons may not have sufficient energy to escape completely the electrostatic field of the parent ion and are drawn back to produce highly excited water molecules which dissociate into hydrogen atoms and hydroxyl radicals.



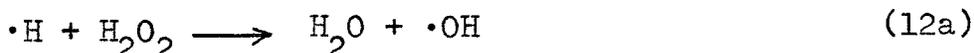
Alternatively, excited water molecules may dissociate or lose their excess energy through collisions with other molecules.



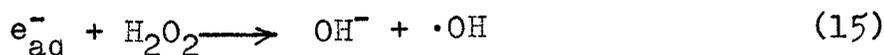
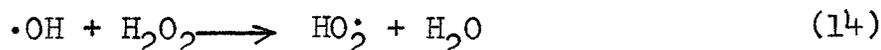
Various models have been presented to account for the radicals formed and their distribution in the system. Although the models differ in certain respects they all predict hydrogen atoms,

hydrated electrons, and hydroxyl radicals initially distributed in or near spurs spaced along the track of the primary ionizing electron in a similar manner to the original ions and excited molecules. About 10^{-11} seconds after the passage of the γ -ray photon the spurs have a diameter of about 20 \AA and contain an average of 2.5 to 5 radical pairs. The spurs are spaced along the track at relatively large intervals of the order of 5000 \AA (8). The radical concentration within the spur is about 1 M.

There is competition between diffusion and recombination within the spur until after about 10^{-8} seconds the spur is sufficiently large for radical-radical recombination to be negligible. At this point the amounts of hydrogen atoms, hydroxyl radicals, and hydrated electrons present or reacted with the solute are usually referred to as the primary radical yields. The amounts of any compound formed by radical recombination are referred to as primary molecular yields. The following radical recombinations may occur to produce the identifiable molecular products H_2 and H_2O_2 (9, 10, 11).



In the absence of radical scavengers the molecular products H_2 and H_2O_2 are susceptible to radical attack according to reactions (13) to (15).



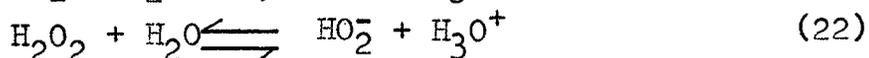
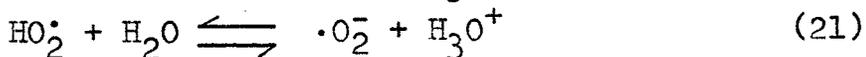
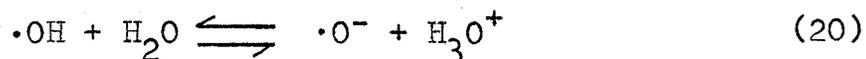
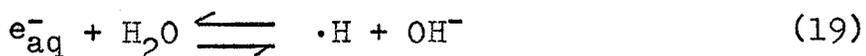
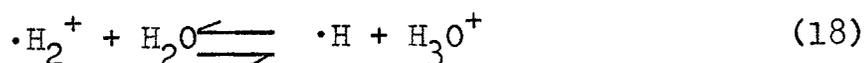
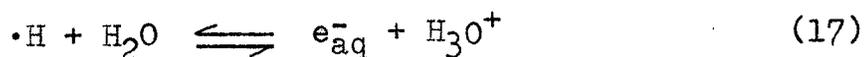
The radical $\text{HO}_2\cdot$ disproportionates to form H_2O_2 and $\text{O}_2\cdot$.



The primary yields as well as all yields from radiation-induced chemical reactions are usually expressed as G values. This quantity is defined as the number of particles formed or destroyed per 100 eV absorbed by the system. G_x denotes the primary yield of a reactive intermediate; $G(x)$ denotes the measured yield of a final product. The primary radical yields are usually measured by

scavenger techniques and are found to be slightly dependent upon the nature and concentration of the scavenger. This topic is reviewed by Buxton (12). The relative reaction rates of a radical with various solutes can be determined by allowing the solutes in several different ratios to compete for the radical and determining the extent to which each reacts. Often, absolute reaction rates can be measured by pulse radiolysis or by flash photolysis.

There has been some controversy over the effects of pH on the primary radical and molecular yields (12, 13). The primary radicals are subject to the following acid-base equilibria:



If these equilibria and all possible radical reactions are carefully considered in the mechanism and if all measureable products are determined to check the mechanism then the only changes in the primary yields are increases in the radical yields

below pH 3 (13). This increase is probably due to reaction (17). The hydrogen atoms formed are very small, are ^{not} solvated, and diffuse 8 to 10 times faster than their conjugate species, the hydrated electron (12). The hydrogen atoms thus stand a much better chance of leaving the spur and reacting with solute molecules than do the hydrated electrons.

Draganić et al. have obtained the following values for the primary radical and molecular yields for the range $3 < \text{pH} < 13$ (13).

$$\begin{aligned} G_{-\text{H}_2\text{O}} &= 4.09 \\ G_{\text{H}} + G_{e_{\text{aq}}^-} &= 3.18 \\ G_{\text{OH}} &= 2.72 \\ G_{\text{H}_2} &= 0.45 \\ G_{\text{H}_2\text{O}_2} &= 0.68 \end{aligned}$$

There is substantial evidence for $G_{\text{H}} \cong 0.6$ (12) and thus $G_{e_{\text{aq}}^-} \cong 2.58$. These values all meet the requirements of material balance and will be used throughout this work.

$$G_{-\text{H}_2\text{O}} = G_{\text{OH}} + 2G_{\text{H}_2\text{O}_2} = G_{e_{\text{aq}}^-} + G_{\text{H}} + 2G_{\text{H}_2} \quad (23)$$

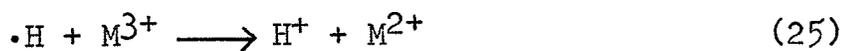
The primary radical species may react with the added solutes in a number of ways.

The hydrogen atom may act as an oxidizing agent

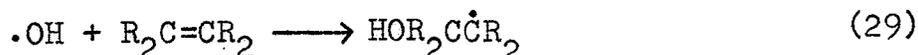
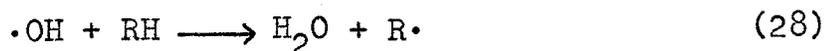
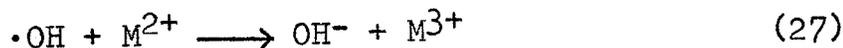
and abstract another hydrogen atom from an organic substrate.



Alternatively it can behave as a reducing agent by donating an electron or adding to an unsaturated organic substrate.



The hydroxyl radical acts solely as an oxidizing species either by removing electrons or by hydrogen atom abstraction or by addition to unsaturated substrates.

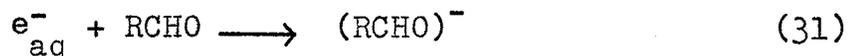


The hydrated electron reacts as a reducing agent by adding to a cation or some other compound.

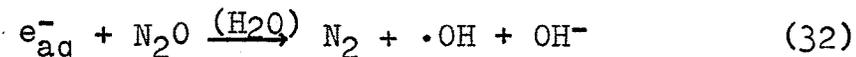


In general, the solvated electron can only add to a compound if it has vacant, low-energy orbitals capable of accepting the electron without unreasonable excitation. Systems containing π bonding such as olefins and carbonyl

compounds generally have such orbitals available.



Saturated compounds such as water with no vacant orbitals react very slowly if at all. One of the compounds used quite frequently to scavenge hydrated electrons is nitrous oxide. This compound reacts rapidly with the electrons and converts them into hydroxyl radicals.



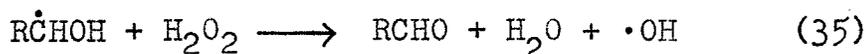
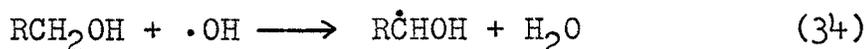
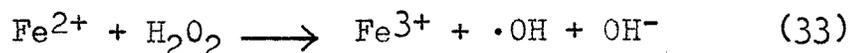
B. Free Radical-Induced Oxidation of Simple Organic Compounds by Hydrogen Peroxide.

Several organic compounds have been oxidized by hydrogen peroxide in chain reactions involving a number of modes of initiation.

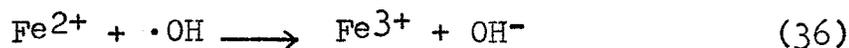
1.2 Metal Ion/H₂O₂ Initiation

Mertz and Waters (14, 15) have proposed a chain mechanism to explain Fenton's reaction i.e. the oxidation of polyhydric alcohols, α -hydroxy acids and carbohydrates by cold hydrogen peroxide in the presence of a ferrous salt. These reagents have also been shown to oxidize the monohydric alcohols ethanol, methanol, and 2-propanol by an analogous mechanism which is shown below.

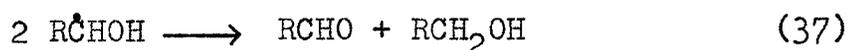
Chain initiation.



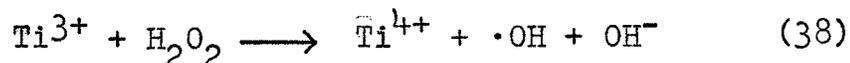
Chain termination at low alcohol concentrations:



Chain termination at high alcohol concentrations:



Norman and West (16) have studied the Fenton and Ti (III) /H₂O₂ systems by fast-flow e.s.r. techniques. The Ti (III) /H₂O₂ system behaves in a similar fashion to the Fenton system. Initially Ti (III) ions react with H₂O₂ to give hydroxyl radicals.

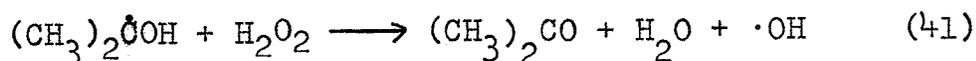
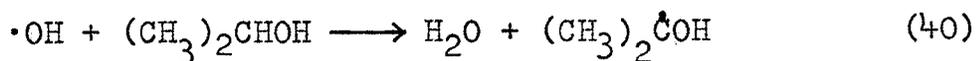


If any readily oxidized compound is also present, the ·OH radical will abstract a hydrogen atom from it to produce a radical which can be detected by e.s.r. Hydrogen peroxide is of special interest because further ·OH radicals are produced when the H₂O₂ oxidizes the organic radical thus sustaining a chain reaction.

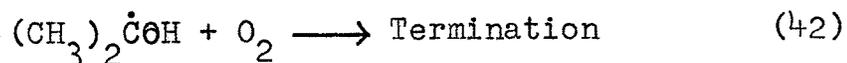
1.3 Thermal Initiation

Acetone is formed by the reaction bet-

ween 2-propanol and hydrogen peroxide. When oxygen-free nitrogen was passed through 2-propanol and 30% H_2O_2 at $78^\circ C$ a rapid decrease in the concentration of H_2O_2 and 2-propanol was noted (17, 18). It was believed that the oxidation occurs via a free radical chain mechanism.



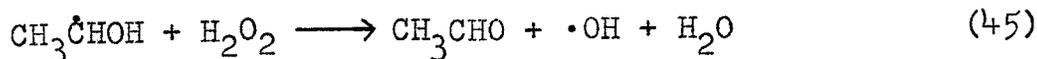
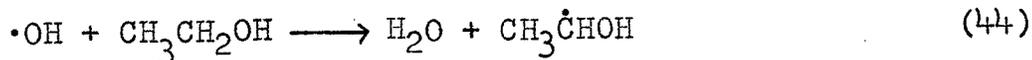
In oxygenated systems the oxygen would react with the organic radical to terminate the chain.



No termination reaction was suggested for deaerated systems.

1.4 Photochemical Initiation

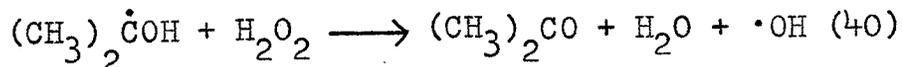
Baxendale and Wilson (19) have studied the photolysis of hydrogen peroxide in degassed solution at high light intensities. Formic acid, carbon monoxide, ethanol, and 2-propanol were found to induce the chain decomposition of hydrogen peroxide. With ethanol, acetaldehyde was the major, if not the only, oxidation product. The authors suggested the following chain mechanism to account for its production.



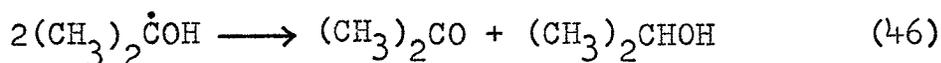
No termination reaction was offered but if the mechanism is analogous to that for the chain oxidation of formic acid as the authors suggest then the termination step must involve a reaction between the organic radical and a hydroxyl radical.

1.5 Radiation Chemical Initiation

In an investigation of the primary radical yields in deaerated aqueous solutions of 2-propanol containing nitrous oxide, Allan and Beck (20) detected molecular hydrogen peroxide in low stationary-state concentration in both neutral and acidified solutions. This result was obtained when either Co^{60} γ -rays or low dose rate electron radiations were used as an energy source. The disappearance of H_2O_2 was accounted for by a chain process involving the reaction of the organic radical with H_2O_2 according to reaction (40).

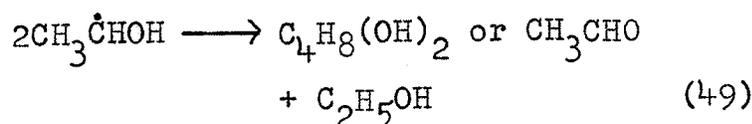
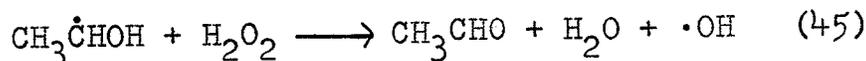
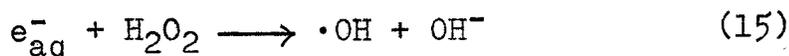
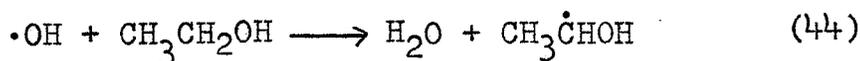
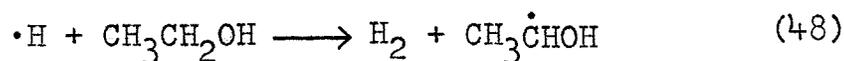
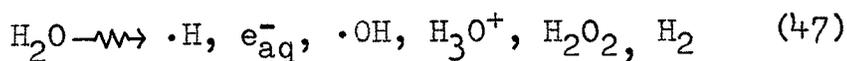


Reaction (40) is in competition with reaction (46) in which the organic radical disproportionates to give acetone.



The formation of pinacol by the combination of two organic radicals apparently does not occur in aqueous solution.

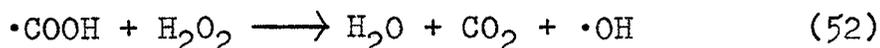
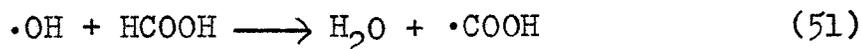
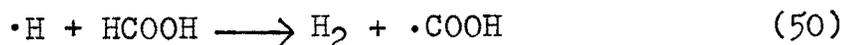
Seddon and Allen (21) discovered that peroxide disappeared with a high yield when aqueous ethanol solutions containing H_2O_2 were irradiated with Co^{60} γ -rays. The authors attributed this result to the following chain mechanism:



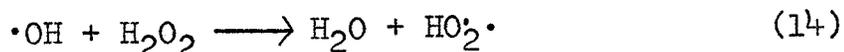
They concluded that disproportionation to aldehyde and alcohol occurred in about 30% of the termination reactions. Using the rotating sector method Seddon and Allen obtained a value of $1.5 \times 10^5 \text{ M}^{-1} \text{ sec.}^{-1}$ for k_{45} .

Formic acid solutions containing hydrogen peroxide were found to react by a chain mechanism

when exposed to ionizing radiation. The propagation steps suggested by Hart (22) were:



Reaction (14) was believed to be the termination step because increasing the peroxide concentration reduced the yield of CO_2 and the hydroperoxy radical does not propagate the chain.



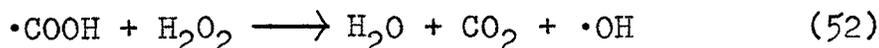
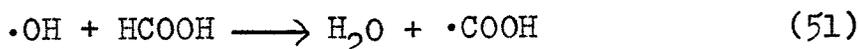
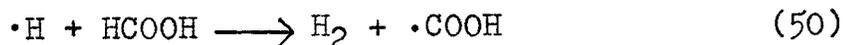
1.6 Summary

The free radical oxidation of several organic solutes including ethanol and 2-propanol by hydrogen peroxide has been studied. The primary radicals were produced by:

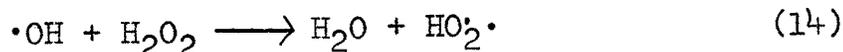
- (1) the reaction of a metal ion with H_2O_2
- (2) the thermal decomposition of H_2O_2
- (3) the photolysis of H_2O_2
- (4) the radiolysis of water

Typically, the primary radicals, $\cdot\text{H}$ and $\cdot\text{OH}$, abstracted a hydrogen atom from the organic solute. This initiation step was followed by a reaction between the resulting organic radical and hydrogen peroxide to form the oxidized product and an $\cdot\text{OH}$

when exposed to ionizing radiation. The propagation steps suggested by Hart (22) were:



Reaction (14) was believed to be the termination step because increasing the peroxide concentration reduced the yield of CO_2 and the hydroperoxy radical does not propagate the chain.



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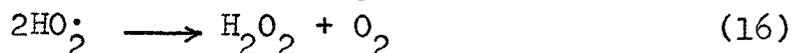
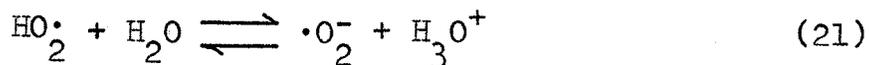
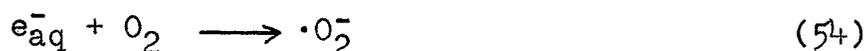
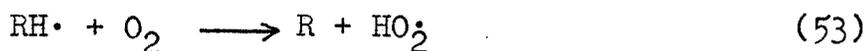
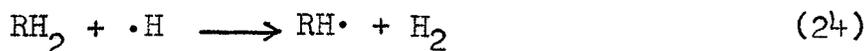
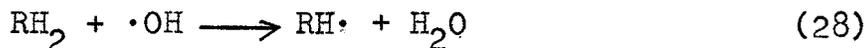
radical which may propagate the chain. The chains were terminated either by a combination or disproportionation of two organic radicals or by a reaction between a primary radical and H_2O_2 or oxygen.

C. Radiation - Induced Oxidation of Simple Organic Compounds in Aerated Aqueous Solutions

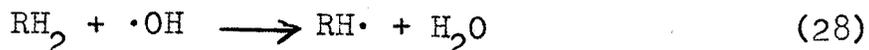
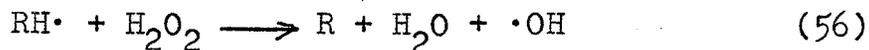
When dilute aqueous ethanol solutions which had been air-saturated were exposed to x-rays both acetaldehyde and hydrogen peroxide were found to be formed (23). Hydrogen peroxide was produced at a rate linear with dose up to a total dose of 8×10^{-6} eV/N per ml. followed by a rapid decrease in yield. The maximum peroxide concentration was about 2.7×10^{-4} M. Van Buskirk (24) has irradiated aerated solutions of 2-propanol, isopropylamine, and di-isopropylamine and shown that hydrogen peroxide is formed as described for ethanol. Acetone was produced at about the same rate in all cases. The acetone concentration increased linearly with dose up to the region where the peroxide curve peaked after which an increase in the rate of acetone formation was noted. A similar pattern of peroxide production and subsequent destruction was observed for several

other organic solutes. When a glucose solution was oxygen saturated a maximum concentration of 4.9×10^{-4} M peroxide was obtained from a dose of 1.75×10^{22} eVl⁻¹. This result was an increase of 350% over the air-saturated system.

The mechanism of Garrison (25) appeared to be valid as long as oxygen remained in the solutions.



As the concentration of oxygen approached zero and the concentration of hydrogen peroxide built up, the organic radicals attack the peroxide in preference to the oxygen giving rise to a chain reaction.



These reactions continue until the chain is terminated either by a combination or disproportionation of two organic radicals or by a reaction between a primary radical and an organic radical.

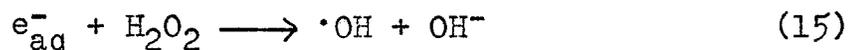
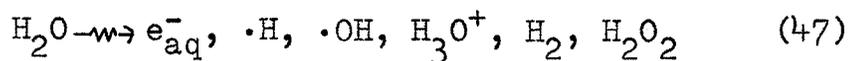
D. Radiation - Induced Oxidation of Alcohols
by Hydrogen Peroxide in Deaerated Aqueous
Solutions

Earlier in this introduction the work of Allan and Beck (20) was discussed on the radiation-induced disappearance of hydrogen peroxide in aqueous 2-propanol solutions containing N_2O . Also discussed were the observations of Seddon and Allen (21) concerning the radiation-induced oxidation of ethanol solutions containing hydrogen peroxide. In both cases mechanisms, in which the radicals, $CH_3CHOH\dot{C}H_2$ and $\dot{C}H_2CH_2OH$, were not considered, were offered to explain the reactions. However, Burchill and Ginns (26) have reinvestigated the $H_2O_2/2$ -propanol system and shown that certain features of the dependence of the yields on solute concentration are inconsistent with the mechanism proposed above.

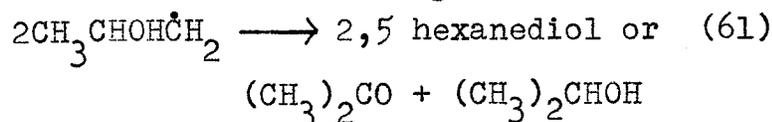
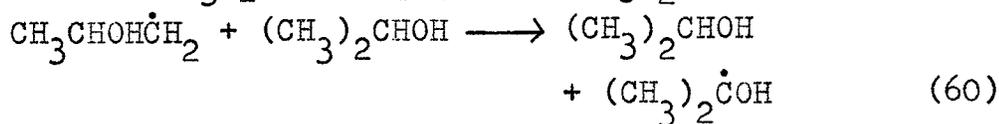
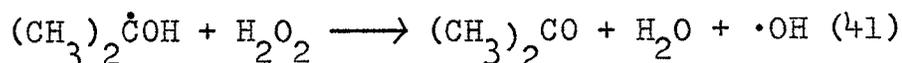
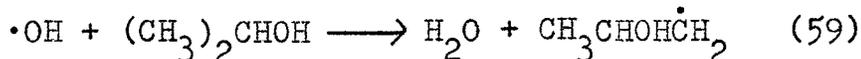
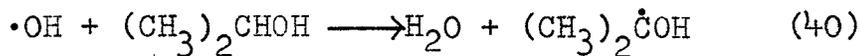
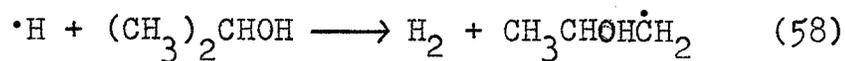
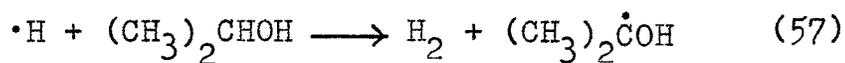
The rate of hydrogen peroxide destruction was independent of its concentration in the range

5×10^{-2} M to 10^{-3} M but was stoichiometrically equivalent to the acetone formation in those systems where both quantities were measured. In the range 0.13 M to 1.05 M 2-propanol $G(-H_2O_2)$ and $G(\text{acetone})$ both increased linearly with increasing alcohol concentration. Extrapolating the curve gives significant chain values of $G(-H_2O_2)=33.4$ and $G(\text{acetone})=31.2$ at zero 2-propanol concentration. An increase in $G(\text{acetone})$ with decreasing dose rate was clearly demonstrated.

In order to account for these experimental observations the following mechanism was proposed for solutions 0.1 M to 1.0 M 2-propanol and 5×10^{-2} M to 10^{-3} M H_2O_2 .



At the concentrations used all the $\cdot H$ and $\cdot OH$ radicals react with the 2-propanol. Whereas previous authors (20, 21) had assumed that the hydrogen atom abstraction occurred only at the α -position of the alcohol, Burchill and Ginns suggested that this abstraction might also occur at the β -position.

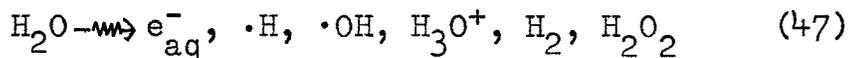


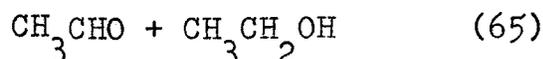
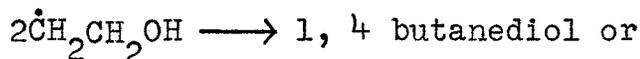
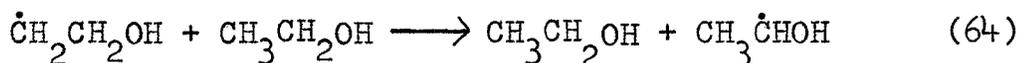
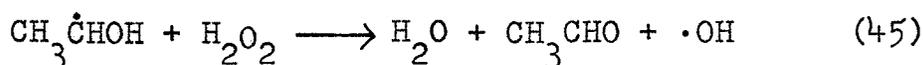
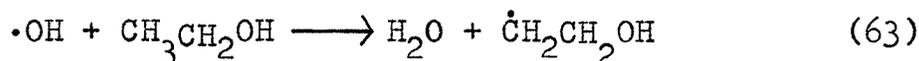
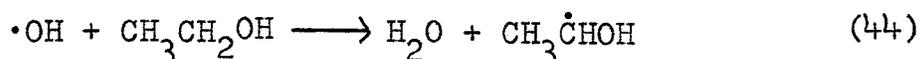
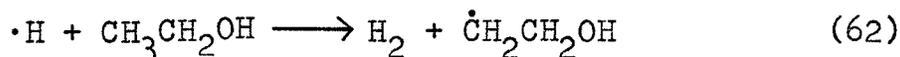
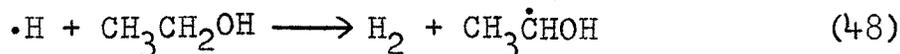
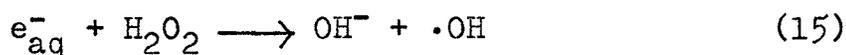
Also notable in their mechanism is the radical conversion reaction (60). The dependence of the yields on alcohol concentration was thus explained by a competition between a radical terminating reaction and a reaction of that radical with the alcohol.

The yield expression derived from the mechanism predicts a linear dependence of the yields on 2-propanol concentration, no dependence on H_2O_2 concentration, and a non-zero intercept at zero alcohol concentration all as observed experimentally. Although an exact

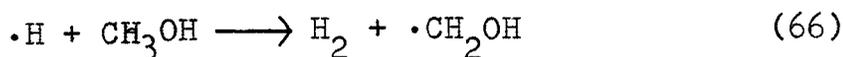
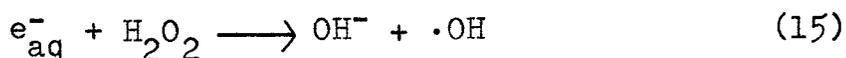
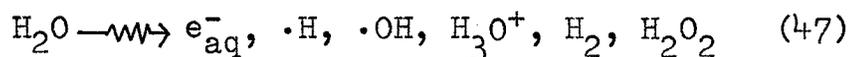
inverse square root dose rate effect as predicted by the mechanism was not observed, the very fact of a significant dose rate effect indicated that there is a bi-molecular termination.

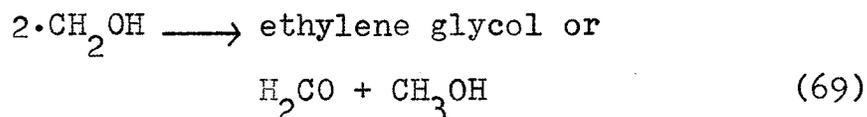
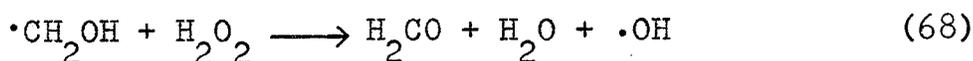
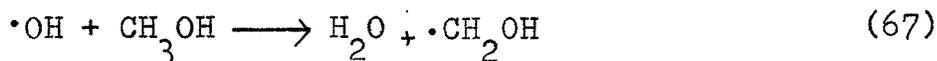
In order to test their mechanism further, Burchill and Ginns (27) irradiated aqueous solutions of ethanol and methanol in the presence of hydrogen peroxide. It is possible for ethanol to form both α and β radicals whereas methanol can form only an α radical. In the case of ethanol results similar to those obtained for 2-propanol were observed. For solutions containing 0.085 M to 0.85 M ethanol the rate of H_2O_2 removal was independent of its concentration below 0.02 M. Acetaldehyde was formed in stoichiometrically equivalent yields and both $G(\text{acetaldehyde})$ and $G(-H_2O_2)$ increased linearly with alcohol concentration. Extrapolation to zero alcohol concentration gave an intercept of $G(-H_2O_2)=45.4$ and a significant dose rate effect was also noted. The following mechanism, analogous to that for 2-propanol, was proposed:





In the case of methanol somewhat different results were obtained. Formaldehyde formation and peroxide destruction were equivalent but dependent on peroxide concentration at all methanol concentrations examined. $\log [\text{H}_2\text{O}_2]$ was a linear function of irradiation time indicating a first order dependence on peroxide concentration. A square root dependence on dose rate was observed. Thus the results conformed to the simple mechanistic scheme suggested prior to the work of Burchill and Ginns (20, 21).





Thus, Burchill and Ginns have shown that in systems where both α and β attack can take place β attack is significant and the rate controlling step is $\beta + \text{alcohol} \rightarrow \alpha + \text{alcohol}$ in competition with $2\beta \rightarrow$ termination. The α radical only is oxidized by the peroxide. As one would expect methanol which has no β hydrogens obeys a simple mechanistic scheme.

On the basis of the foregoing discussion one might expect a small, symmetrical molecule like ethylene glycol to follow the simple mechanistic scheme. One might expect the hydrogen and hydroxyl radicals to attack the ethylene glycol to produce $\dot{\text{C}}\text{HOHCH}_2\text{OH}$ radicals which could then be oxidized to glycolaldehyde by the peroxide or react with an identical radical in a termination step. There is always the possibility that further thermal oxidations could result in products such as glycolic acid, glyoxylic acid, oxalic acid or even carbon dioxide. However, when an aqueous ethylene glycol/ H_2O_2 system was irradiated, acetaldehyde was found

as a major product (28). This compound cannot be accounted for by the simple mechanism. The object of this work has been to investigate the radiation-induced oxidation of ethylene glycol by H_2O_2 with a view to establishing a reaction mechanism to account for the observation of acetaldehyde as a major product.

2. Experimental

2.1 Materials

Water used for making solutions and cleaning glassware was purified by redistillation of the laboratory supply, first from alkaline KMnO_4 solution, and then from acidic $\text{K}_2\text{Cr}_2\text{O}_7$. The distillation apparatus is illustrated in Fig. 1 of reference (29).

H_2O_2 (Fisher Reagent 30%) was used as received as the oxidizing agent.

HClO_4 (Baker and Adamson ACS 70%) was used to acidify the solutions.

$\text{CH}_2\text{OHCH}_2\text{OH}$ (Fisher certified), $\text{CH}_3\text{CHOHCH}_2\text{OH}$ (Fisher USP), $\text{CH}_3\text{CHOHCHOHCH}_3$ (K&K Laboratories, Inc.) $\text{CH}_2\text{OHCH}_2\text{CH}_2\text{OH}$ (Eastman Organic Chemicals) were used without further purification in the sample preparation.

All chemicals used for dosimetry and analysis were of Reagent Grade quality and used as received.

2.2 Irradiation Facilities

The source of γ -rays was a Gammacell 220 unit installed by Atomic Energy of Canada Limited. The active Co^{60} is contained in pencils arranged vertically around the cylindrical sample chamber which is 6 inches in diameter and 8 inches in height. The dose varies somewhat with position in the sample chamber but reproducible positioning of samples was ensured by the use of sample holders described elsewhere (29). When installed (May 1966) the dose rate measured in the central field by the Fricke dosimeter (30) was $1.6 \times 10^6 \pm 2.2\%$ rads/hr. For dose rate studies the dose rate was reduced to 26.8% of the unattenuated value by fitting a hollow lead cylinder inside the sample chamber.

For experiments involving photochemical initiation the light source was a Hanovia Z 1500-108 low pressure mercury arc with a Vycor envelope. Hydrogen peroxide is the absorbing species at 2537 Å.

2.3 Dosimetry

The Fricke dosimeter (30) was used to determine the dose rates from the Gammacell.

This dosimeter consists of an air-saturated aqueous solution containing 10^{-3} M ferrous ammonium sulfate and 0.4 M sulfuric acid. Ten ml. aliquots of this solution were placed in irradiation cells and irradiated for various times. The concentration of the ferric ion produced upon irradiation was measured spectrophotometrically against a blank of unirradiated dosimeter solution at 305 nm by means of a Carl Zeiss PMQ II spectrophotometer. The extinction coefficient for ferric ion at about 25°C in an unthermostated cell holder was taken to be $2.2 \times 10^3 \text{ M}^{-1} \text{ cm.}^{-1}$. $G(\text{Fe}^{3+})$ was assumed to equal 15.6 ions per 100 eV of dose absorbed. The dose rate was checked periodically but in practice once the dose rate had been established the value for a particular month was determined using a half-life of 5.27 years for Co^{60} .

Energy absorption due to Compton scattering of γ -rays is proportional to the electron density of the absorbing medium. Consequently it was necessary to correct the dose measured by the Fricke dosimeter for the electron density of the samples. Sample calculations of true absorbed dose rates for various solutions has been carried out (29).

In the case of photochemical initiation

the intensity of the absorbed UV radiation was determined in this laboratory by the potassium ferrioxalate actinometer developed by Parker and Hatchard (31). Sulfuric acid solutions of $K_3Fe(C_2O_4)_3$ were irradiated at 2537 \AA and the amount of ferrous ion produced measured spectrophotometrically. Since $\Phi(Fe^{2+})$ is well characterized the intensity of the incident source may be calculated.

2.4 Radiation Cells and Sample Preparation

The pyrex cells used for γ -irradiation were of two types depending on whether the samples were degassed or aerated and have been described elsewhere (24). The cells used when photolysis of H_2O_2 was involved were the same as for γ -irradiation with the addition of a cylindrical fused silica optical cell of 4.2 cm. o.d. and 1.00 cm. light path attached to a side arm. After degassing the solution in the pyrex bulb the solution was tipped into the optical cell where it was irradiated.

The pyrex cells and all glassware for γ -irradiation were first washed with permanganic acid solution. This was followed by a rinsing with aqueous HNO_3 to which a small quantity of H_2O_2 had been added. The photolysis cells were washed with

concentrated HNO_3 . In all cases the glassware was finally rinsed several times with distilled water and triply distilled water. The irradiation cells were then drain dried.

A typical stock solution was prepared by transferring an aliquot of H_2O_2 into a 100 ml. volumetric containing a small amount of triply distilled water. After the flask was weighed an appropriate volume of organic solute was pipetted into the flask and it was weighed again. The solution was then made up to volume with more triply distilled water.

Ten ml. of stock solution was pipetted into each irradiation cell and the cells were attached by the top assembly to a vacuum line if degassing was necessary. The vacuum line was constructed of pyrex glass and included an oil diffusion pump. Apiezon N grease was used for all seals. The samples were degassed by four cycles of freezing, pumping, and thawing. A mixture of solid CO_2 and acetone or, on occasion, a mixture of liquid N_2 and ethanol was employed to freeze the samples. When N_2O was used it was allowed to equilibrate

with the sample at a known pressure before the cells were sealed off and removed from the vacuum line. The N_2O was kept in a storage bulb joined to the vacuum assembly and its concentrations in the samples were calculated according to the method described in reference (32). When oxygenation was required oxygen was simply bubbled through the sample for about ten to fifteen minutes.

Samples were positioned reproducibly in the irradiation chamber with the aid of sample holders and were irradiated for known times using the timing device incorporated into the Gammacell. No thermostating of samples was attempted.

In the case of photolysis of H_2O_2 the silica cells were placed in a holder to ensure a reproducible position relative to the source. The timing was controlled manually with a stop watch. In all experiments the samples were analyzed upon completion of the irradiation.

2.5 Analytical Techniques

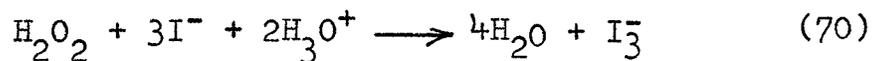
Spectrophotometric techniques proved unsatisfactory for the determination of acetaldehyde, the main product formed when aqueous ethylene glycol was irradiated. Thus gas chromatography

was used in all measurements of acetaldehyde concentration. The acetaldehyde was readily separated from the ethylene glycol and other compounds using a Victoreen 4001 chromatograph with a 6 ft. column (1/8 inch diameter) packed with Chromosorb 102. Helium was used as the carrier gas with a flow rate of about 10 ml./min. and in all analyses the column temperature was maintained close to 120°C. Detection was accomplished by means of flame ionization. The acetaldehyde peaks were quite uniform and their areas were readily and accurately determined. The areas of the peaks were compared with that of a standard solution whose concentration was accurately known. In this fashion an accuracy of about $\pm 5\%$ was attained in all individual measurements.

Methyl ethyl ketone was determined in the same way as acetaldehyde except the column temperature was maintained at about 180°C. When the propylene glycol system was examined a column packed with 2% Carbowax 20M on 60/80 Chromosorb W was used.

All remaining measurements were made spectrophotometrically at room temperature and were accomplished with a Carl Zeiss PMQ II spectrophotometer. The destruction of H_2O_2 was followed by the triiodide

method (33). Five ml. of solution A, containing 1.25 g. NaOH, 41.5 g. KI, and 0.125 g. $(\text{NH}_4)_6\text{Mo}_7\text{O}_{25}\cdot 4\text{H}_2\text{O}$ in 500 ml. water was mixed together with 5 ml. of solution B, containing 12.5 g. KH phthalate in 500 ml. water. An aliquot of sample was added and the whole diluted to 25 ml. with water. The color development was immediate and the reaction is as follows:



The product, I_3^- , absorbed at 350 nm. Its extinction coefficient has been measured in this laboratory and found to be $2.38 \times 10^4 \text{ M}^{-1}\text{cm.}^{-1}$ (24).

Glycolaldehyde was determined by adding 2 ml. of 2,4-dinitrophenylhydrazine reagent to an aliquot of sample and letting the mixture stand for two hours (34, 35). The reagent was prepared by dissolving 0.1 g. 2,4-dinitrophenylhydrazine in 2N HCl to a concentration of 20 /ml. When the mixture had stood for two hours 500 γ 4% NaOH solution was added and the whole diluted to 10 ml. with ethanol. The glycolaldehyde content was then calculated from the optical absorption of the 2,4-dinitrophenyl hydrazone at 600 nm.

Glycolic acid, produced by the reduction

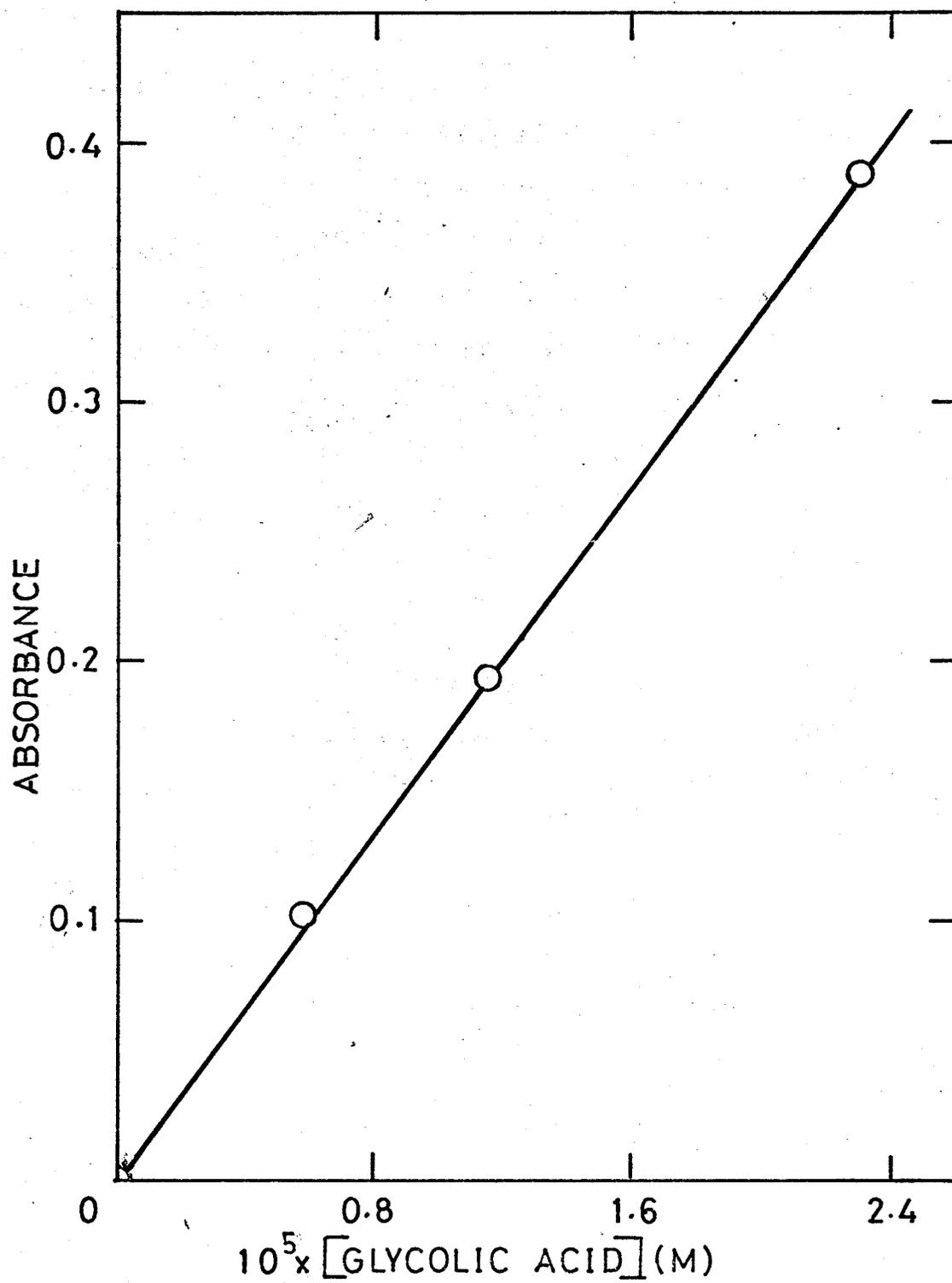
of H_2O_2 , was determined by the chromotropic acid method (36). An aliquot of sample along with 0.5 ml. of 5% chromotropic acid was added to 20 ml. of sulfuric acid. The mixture was heated to 100°C for 30 minutes, cooled to room temperature, and diluted to 25 ml. with concentrated sulfuric acid. The complex formed absorbs at 570 nm. with an extinction coefficient of $1.68 \times 10^4 \pm 2\% \text{ mole}^{-1} \text{ cm.}^{-1}$ (see Fig. 1). This method cannot distinguish between glycolic acid and formaldehyde but glycolic acid is the more likely product. The basic mechanism that is proposed is unchanged whether the oxidation product is glycolic acid or formaldehyde.

Acetone, one of the products formed when aqueous propylene glycol was irradiated, was determined by the method of Berntsson (37). One ml. concentrated NaOH (425 g. per l.) and an aliquot of sample were diluted to about 10 ml. with water. Then 250 μl . salicylaldehyde was added and the solution was well shaken. Finally, 10 ml. concentrated NaOH was added and the whole was diluted to 25 ml. with water. After two hours formation of the acetone-salicylaldehyde complex was complete. Its extinction coefficient at 474 nm. was taken to be $1.80 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ (24).

Fig. 1

Calibration curve used to determine the extinction coefficient of glycolic acid with 5% chromotropic acid at 570 nm.

FIG. 1



3. Results

A. Ethylene Glycol-H₂O₂ in Deaerated Aqueous Solution

3.1 Acetaldehyde Formation

Aqueous solutions 0.01 M in hydrogen peroxide and containing ethylene glycol in concentrations ranging from 0.18 M to 1.8 M were vacuum degassed and irradiated with γ -rays up to a total dose of $5.3 \times 10^{22} \text{ eV l}^{-1}$. A typical dose-yield plot for the acetaldehyde produced is shown in Fig. 2. A characteristic feature of all such plots is their failure to pass through the origin. The G values obtained from the slopes of these lines are tabulated in Table 3.1.

Table 3.1

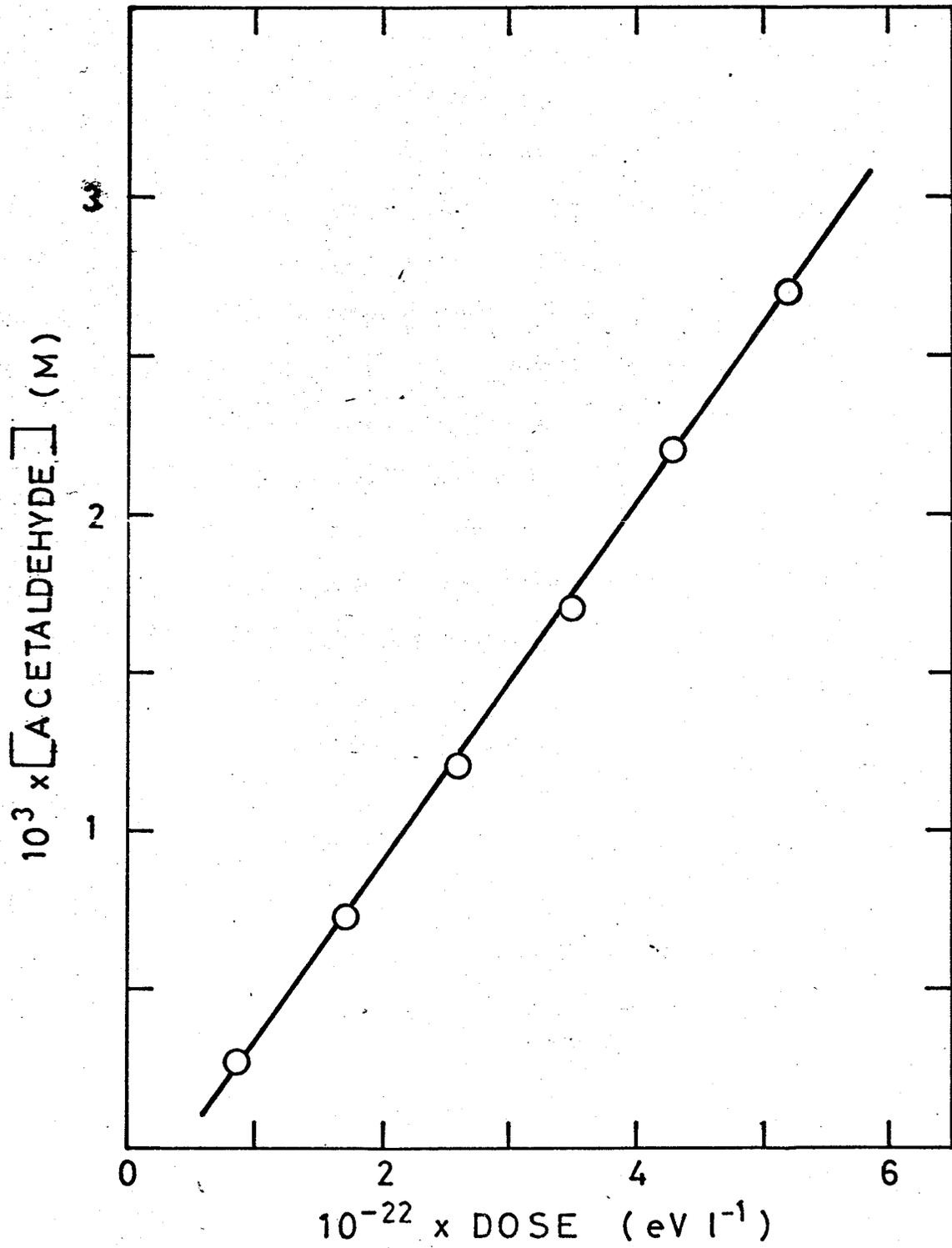
Variation of G(acetaldehyde) with ethylene glycol concentration with 0.01 M hydrogen peroxide present

<u>[ethylene glycol]</u>	G(acetaldehyde)
0.175 M	1.37
0.538 M	3.41
0.897 M	8.04
1.24 M	9.56
1.78 M	13.2

Fig. 2

Acetaldehyde concentration observed in degassed aqueous solutions 0.54 M in ethylene glycol and 0.01 M in hydrogen peroxide for various absorbed doses.

FIG. 2



The data from Table 3.1 are illustrated in Fig. 3. The relatively large value of 13.2 for G(acetaldehyde) indicates that the acetaldehyde is formed by a chain reaction and it can be seen from Fig. 3 that G(acetaldehyde) is linearly dependent upon the ethylene glycol concentration in the particular range studied.

To determine the effect of changing the hydrogen peroxide concentration on G(acetaldehyde) three solutions were irradiated, all 1.8 M in ethylene glycol but containing no hydrogen peroxide, 0.01 M hydrogen peroxide, and 0.02 M hydrogen peroxide respectively. The acetaldehyde yields obtained from these solutions are listed in Table 3.2

Table 3.2

Variation of G(acetaldehyde) with hydrogen peroxide concentration.

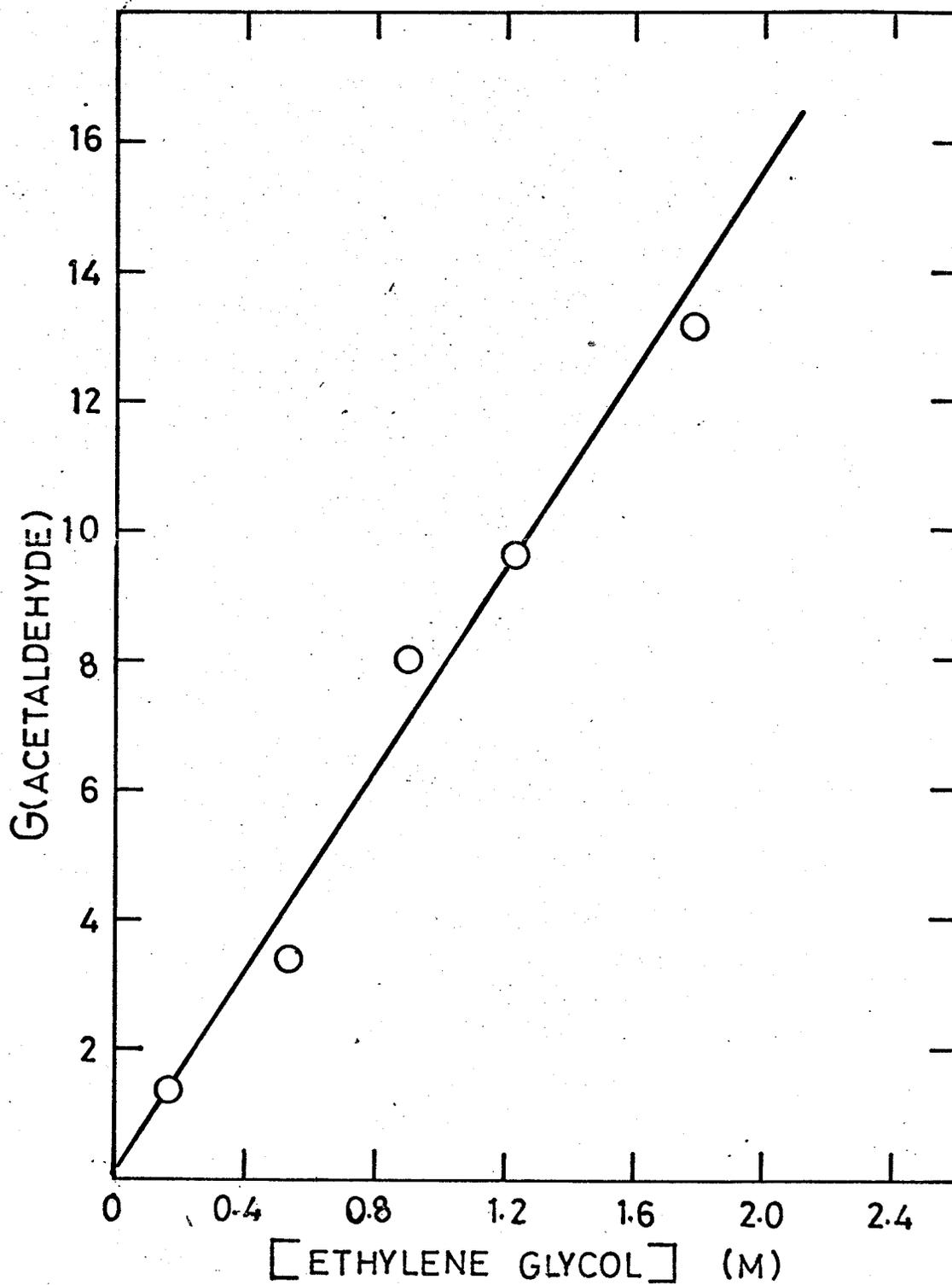
[ethylene glycol]	[hydrogen peroxide]	G(acetaldehyde)
1.77 M	none present	4.31
1.78 M	0.01 M	13.2
1.84 M	0.02 M	13.6

From the information listed in Table 3.2 several conclusions may be drawn. Hydrogen peroxide is

Fig. 3

Variation of G(acetaldehyde) with ethylene glycol concentration. All solutions contained 0.01 M hydrogen peroxide.

FIG. 3



apparently not essential for the reaction to occur although its presence enhances the product yield. Increasing the concentration of hydrogen peroxide from 0.01 M to 0.02 M has no effect on G(acetaldehyde) within experimental error. It would seem that somewhere in the range 0 to 0.01 M hydrogen peroxide reaches its maximum effect on G(acetaldehyde). If Fig. 2 is examined it is apparent that the yield of acetaldehyde is linear with dose even when the dose reaches as high as $5.3 \times 10^{22} \text{ eVl}^{-1}$. When this maximum dose has been absorbed the hydrogen peroxide concentration has been reduced to about $4.3 \times 10^{-3} \text{ M}$. Thus even at this low a concentration of peroxide G(acetaldehyde) is not affected.

3.2 Hydrogen Peroxide Destruction

In order to follow the destruction of hydrogen peroxide a solution 0.877 M in ethylene glycol and 0.01 M in hydrogen peroxide was irradiated to a total dose of $5.2 \times 10^{22} \text{ eVl}^{-1}$. The change in absorbance with irradiation time and in the logarithm of the absorbance with irradiation

time for a given dose rate are shown graphically in Fig. 4. The logarithm of the absorbance evidently varies linearly with irradiation time whereas the absorbance vs. irradiation time plot is definitely non-linear. The destruction of hydrogen peroxide therefore appears to be first order in peroxide. From the slope of the log absorbance vs. irradiation time plot an apparent first order rate constant, k_{app} , was calculated.

The destruction of hydrogen peroxide was followed in solutions 0.01 M in hydrogen peroxide but ranging from 0.18 M to 1.8 M in ethylene glycol. The apparent rate constants calculated for each solution are listed in Table 3.3

Table 3.3

Variation of apparent first order rate constant for hydrogen peroxide destruction with ethylene glycol concentration.

$[\text{ethylene glycol}]$	$10^4 \times k_{app} \text{ (sec}^{-1}\text{)}$
0.177 M	0.840
0.538 M	0.962
0.877 M	1.06
1.24 M	1.18
1.77	1.27

Fig. 4

The destruction of hydrogen peroxide followed spectrophotometrically at 350 nm. in deaerated aqueous solutions containing 0.01 M H_2O_2 initially and 0.54 M ethylene glycol.

Absorbance

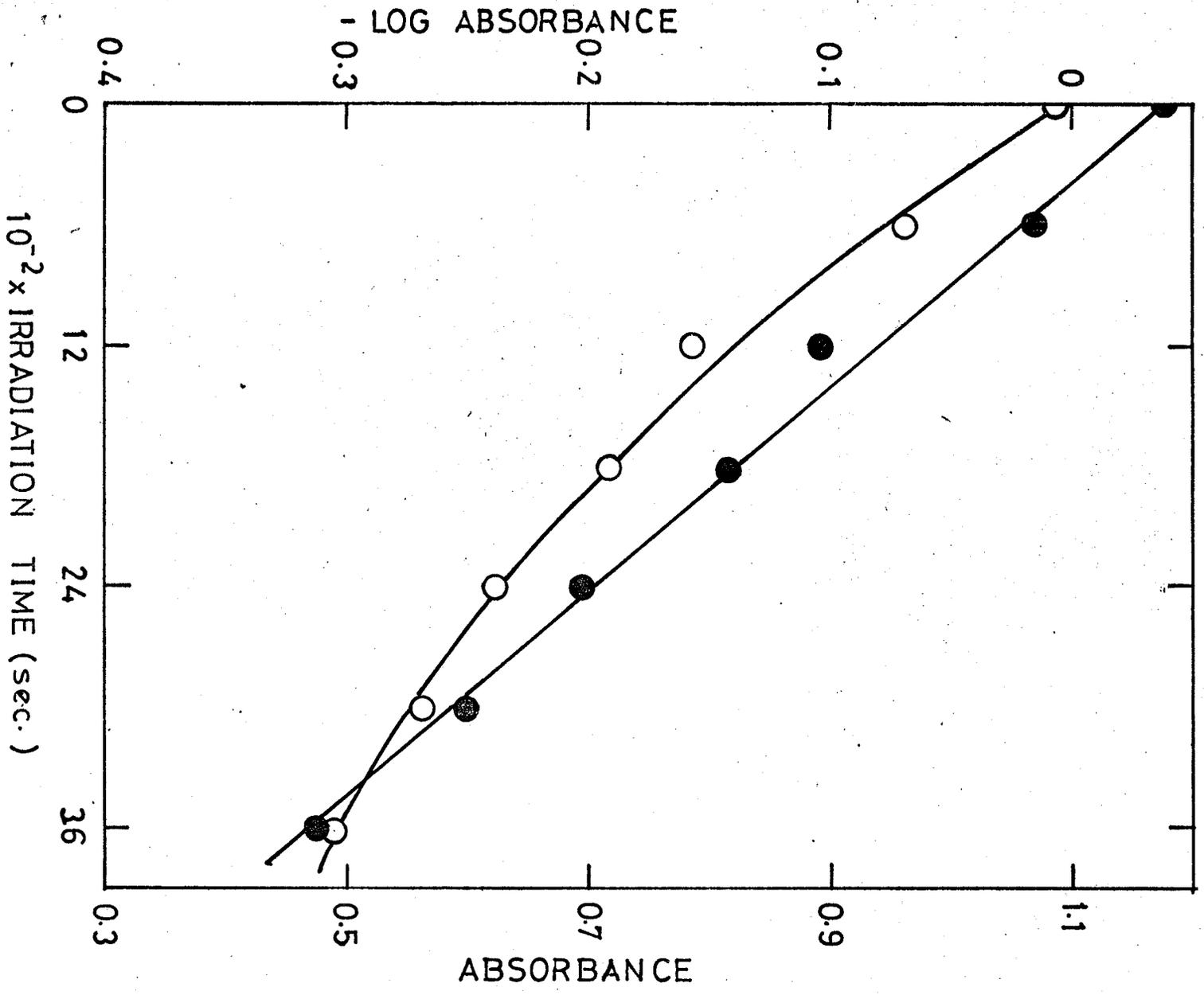


Logarithm Absorbance



The absorbed dose rate was $1.44 \times 10^{19} \text{ eV l}^{-1} \text{ sec}^{-1}$

FIG. 4



The information from Table 3.3 is illustrated in Fig. 5 from which it can be seen that k_{app} varies linearly with ethylene glycol concentration in the range studied.

The effect of changing the initial hydrogen peroxide concentration on the apparent rate constant, k_{app} , is shown in Table 3.4

Table 3.4

Variation of the apparent first order rate constant for peroxide removal with initial hydrogen peroxide concentration.

$[\text{ethylene glycol}]$	$[\text{hydrogen peroxide}]$	$10^4 \times k_{app} \text{ (sec}^{-1}\text{)}$
1.77 M	0.01 M	1.27
1.77 M	0.02 M	0.918

The rate constant is therefore rather insensitive to changes in initial hydrogen peroxide concentration as it changes only by about 25% when the peroxide concentration changes by 100%.

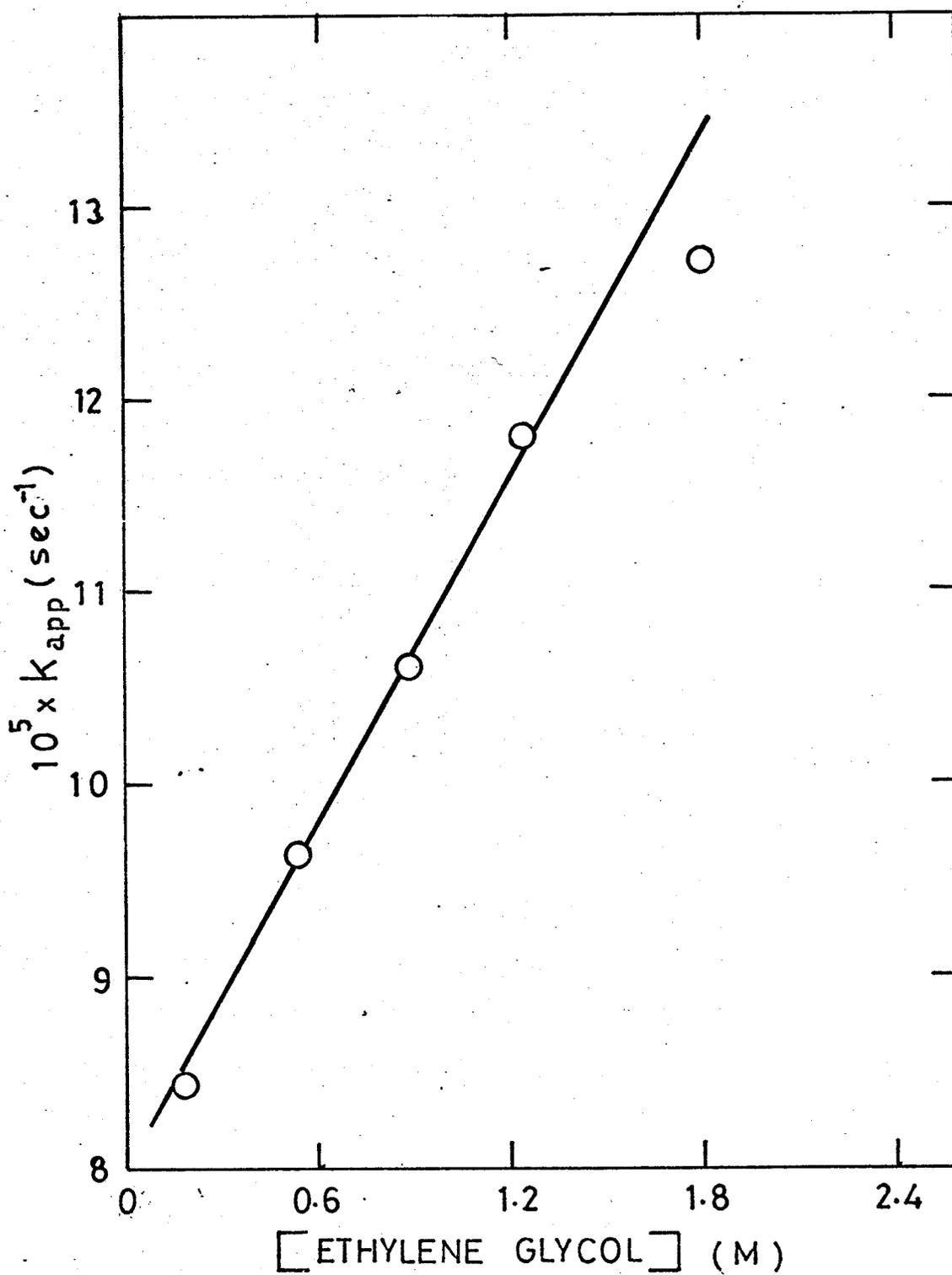
3.3 The Oxidation Product

A possible product for the reaction between ethylene glycol or an ethylene glycol radical and hydrogen peroxide is glycolaldehyde. Although no glycolaldehyde could be detected by the method described in the previous chapter, irradiated

Fig 5

Variation of the apparent first rate constant for hydrogen peroxide destruction, k_{app} , with ethylene glycol concentration. All solutions contained 0.01 M H_2O_2 initially.

FIG. 5



ethylene glycol solutions containing hydrogen peroxide did contain significant amounts of glycolic acid. It is assumed that glycolaldehyde is formed directly but undergoes a further thermal reaction with the peroxide to form glycolic acid. Table 3.5 shows the amount of glycolic acid produced for various irradiation times at a given dose rate.

Table 3.5

Variation of glycolic acid concentration with irradiation time for a dose rate of $1.3 \times 10^{19} \text{ eV l}^{-1} \text{ sec}^{-1}$

[ethylene glycol] = 1.78 M.

$10^3 \times$ [glycolic acid]	irradiation time (min.)
0.23 M	10
0.43 M	20
0.87 M	30
0.95 M	40
1.08 M	50
1.41 M	60

3.4 Summary of the Significant Features of the Reaction

In summary thus far, the significant features of the reaction are as follows:

- (a) Acetaldehyde is formed linearly with dose.
- (b) The reaction has a chain mechanism as indicated by the relatively large values of $G(\text{acetaldehyde})$

- (c) G(acetaldehyde) is linearly dependent on ethylene glycol concentration.
- (d) There appears to be simultaneously a chain reaction producing acetaldehyde and an essentially independent oxidative chain ultimately producing glycolic acid as a major product.
- (e) The destruction of hydrogen peroxide is first order in peroxide.
- (f) The apparent rate constant for peroxide destruction is insensitive to peroxide concentration but is linearly dependent on glycol concentration.

3.5 pH Effects

Only small changes in G(acetaldehyde) were observed as the pH was decreased through the acidic region. These changes were scattered and were attributed mainly to experimental error but in the alkaline region G(acetaldehyde) showed a definite increase. The values obtained are listed in Table 3.6 and illustrated in Fig. 6. All solutions contained 0.01 M hydrogen peroxide.

Fig. 6

Variation of G(acetaldehyde) with pH.
All solutions contained 1.8 M ethylene
glycol and 0.01 M H_2O_2 .

FIG. 6

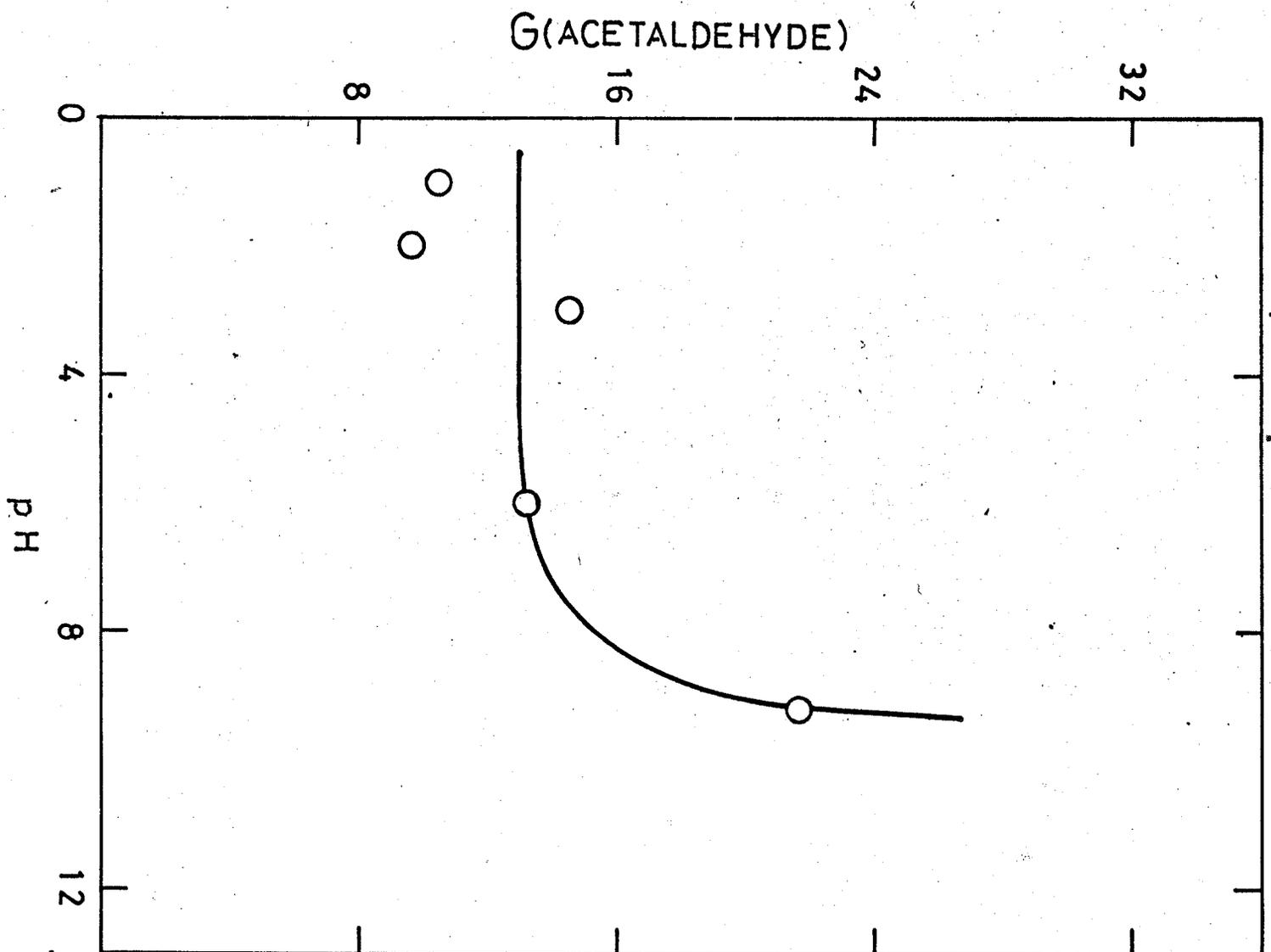


Table 3.6

Variation of G(acetaldehyde) with pH

ethylene glycol	pH	G(acetaldehyde)
1.78 M	1	10.4
1.77 M	2	9.57
1.77 M	3	14.5
1.78 M	6	13.2
1.77 M	9.2	21.6

Seidler and Sonntag, using an ethylene glycol-N₂O system, reported that the pH had an influence on the acetaldehyde yield only in the alkaline region (38).

At pH 1 very little hydrogen peroxide was destroyed after a dose of 5.2×10^{22} eVl⁻¹ had been delivered. As the pH increased, the amount of peroxide destroyed by this dose progressively increased until at pH 9 almost all the peroxide had reacted. This information is presented in Table 3.7 and Fig. 7 in terms of the apparent rate constant for hydrogen peroxide destruction.

Table 3.7

Variation of the apparent rate constant for peroxide removal with hydrogen ion concentration.

Fig. 7

Variation of $\log(10^5 \times k_{app})$ with pH. All solutions contained 0.01 M H_2O_2 initially and 1.8 M ethylene glycol.

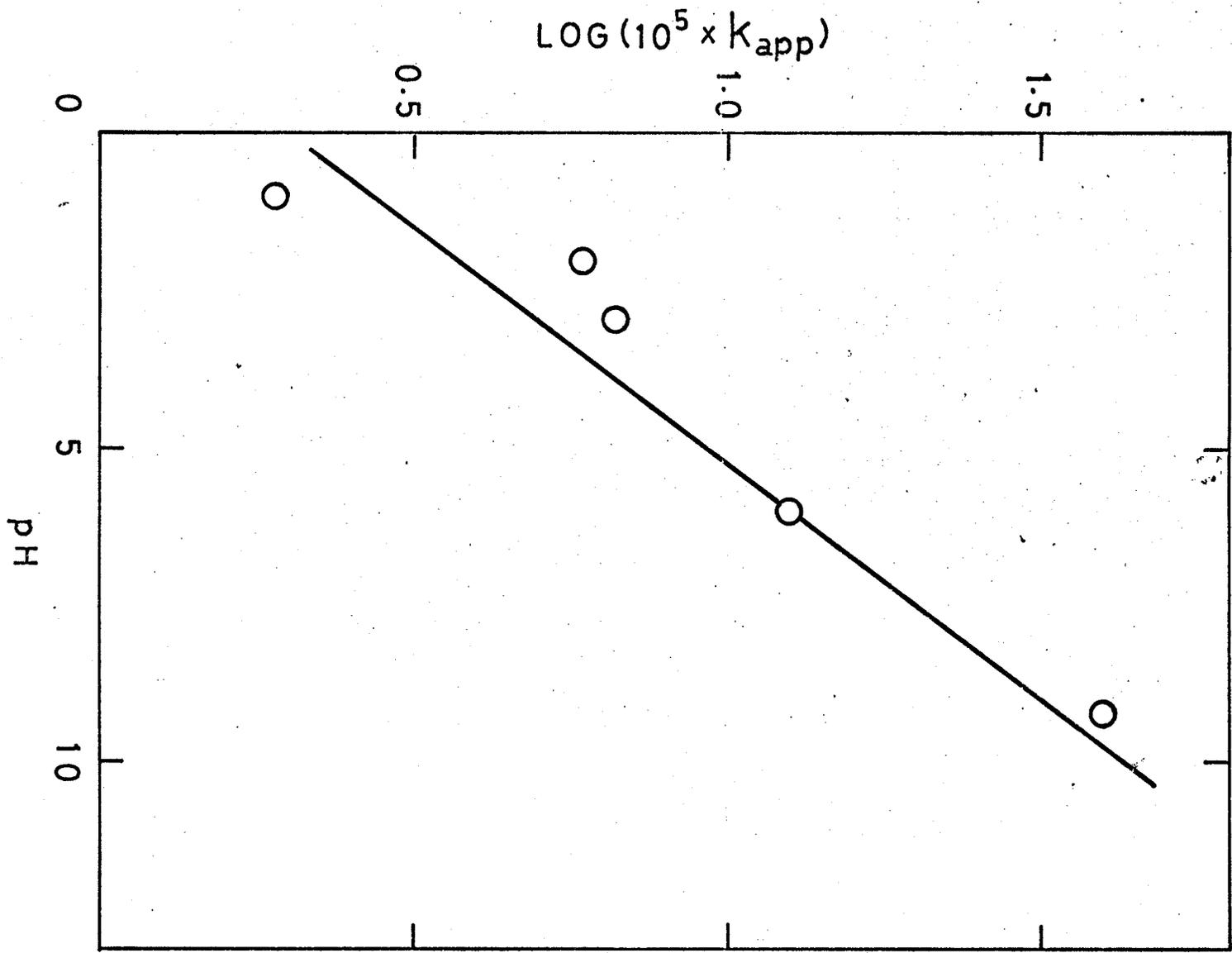


FIG. 7

[ethylene glycol]	[hydrogen ion]	$10^4 \times k_{app} \text{ (sec}^{-1}\text{)}$
1.78 M	10^{-1} M	0.191
1.77 M	10^{-2} M	0.592
1.77 M	10^{-3} M	0.668
1.77 M	10^{-6} M	1.27
1.77 M	10^{-9} M	4.08

Thus, from Fig. 7, the apparent rate constant for peroxide destruction is approximately inversely proportional to the hydrogen ion concentration.

The value of G(acetaldehyde) was obtained for a system at pH 1 but containing no hydrogen peroxide. This G value is compared to a similar system at pH 6 in Table 3.8

Table 3.8

Variation of G(acetaldehyde) with pH with no hydrogen peroxide present.

[ethylene glycol]	[hydrogen peroxide]	pH	G(acetaldehyde)
1.78 M	none	1	16.1
1.84 M	none	6	4.31

It appears therefore that the acetaldehyde formation is catalyzed by acid as well as by hydrogen peroxide.

3.6 Dose Rate Effects

Experiments were performed to discover the

effect of changing the dose rate on G(acetaldehyde) and k_{app} . The dose rate was reduced to about 25% of its normal value by means of lead attenuators. In the case of G(acetaldehyde) an extremely large dose rate effect was observed as is shown in Table 3.9

Table 3.9

Variation of G(acetaldehyde) with dose rate at pH 6

[ethylene glycol]	initial [H ₂ O ₂]	dose rate (eVl ⁻¹ sec ⁻¹)	G(acetaldehyde)
1.78 M	0.01 M	1.46 x 10 ¹⁹	13.2
1.77 M	0.01 M	3.80 x 10 ¹⁸	38.5

The results obtained at pH 1 were similar to those obtained at pH 6.

Table 3.10

Variation of G(acetaldehyde) with dose rate at PH 1

[ethylene glycol]	initial [H ₂ O ₂]	dose rate (eVl ⁻¹ sec ⁻¹)	G(acetaldehyde)
1.78 M	0.01 M	1.43 x 10 ¹⁹	10.4
1.77 M	0.01 M	3.47 x 10 ¹⁸	51.4

When the dose rate was decreased to one-quarter its original value, G(acetaldehyde) increased 2.9 times at pH 6 and 4.9 times at pH 1.

The apparent rate constant for peroxide removal decreased to about 0.4 times its unattenuated value when the dose rate was reduced to one-quarter its normal value as shown in Table 3.11

Table 3.11

Variation of k_{app} with dose rate at pH 6

[ethylene glycol]	initial [H ₂ O ₂]	dose rate (eVl ⁻¹ sec ⁻¹)	$10^4 \times k_{app}$ (sec ⁻¹)
1.77 M	0.01 M	1.45×10^{19}	1.27
1.78 M	0.01 M	3.76×10^{18}	0.513

3.7 Photochemical Initiation

The formation of acetaldehyde was found to occur even more readily when initiated by the photolysis of hydrogen peroxide than by the radiolysis of water. Hydrogen peroxide absorbed ultraviolet radiation at 2537 Å and dissociated into •OH radicals to initiate the chain formation of acetaldehyde. The values of Φ (acetaldehyde), the number of moles of product obtained from one

einstein of photons, observed for both acid and neutral systems are recorded in Table 3.12. The absorbed intensity, I_a was 1.41×10^{-7} einsteins $l^{-1}sec^{-1}$.

Table 3.12

Variation of ethylene glycol	(acetaldehyde) with pH	pH	initial $[H_2O_2]$	Φ (acetaldehyde)
1.77 M		1	0.01 M	9.65
1.77 M		6	0.01 M	8.00

In no instance was more than 16% of the hydrogen peroxide removed during irradiation.

A clearer comparison of acetaldehyde yields obtained under UV and γ -irradiation can be made by examining the chain lengths in both cases. An estimation of the average chain length of a reaction can be made by dividing $\Phi(x)$ or $G(x)$ by the total primary radical yield. The values of the total primary radical yields used in this work are $G_R = 5.9$ (13) and $\Phi_{OH} = 1.0$ (19).

In the case of photoinitiation the average chain length is about 9/1 or 9 molecules of product per primary radical whereas for γ -ray initiation the average chain length is about $13/5.9$ or 2.2. The chain lengths are approximately four times longer

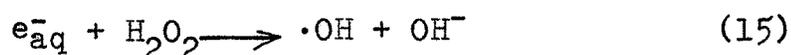
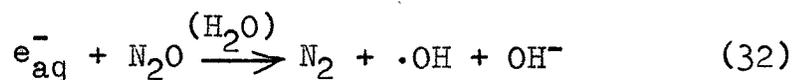
on the average for initiation by peroxide photolysis.

Table 3.12 also shows that changing the pH has little effect on Φ (acetaldehyde) when 0.01 M H_2O_2 is present. A similar result was obtained under γ -ray initiation.

B. Ethylene Glycol- N_2O in Deaerated Aqueous Solution

In order to further examine the chain reaction producing acetaldehyde from ethylene glycol a number of deaerated aqueous solutions of ethylene glycol, all 0.01 M in N_2O , were subjected to γ -irradiation.

Nitrous oxide, like hydrogen peroxide, reacts efficiently with hydrated electrons to produce hydroxyl radicals.



However, it has been demonstrated that no chain oxidation reactions occur in neutral aqueous N_2O solutions containing alcohols like methanol, ethanol, and 2-propanol under γ -irradiation (39).

When a solution 1.8 M in ethylene glycol and 0.01 M in N_2O was irradiated, acetaldehyde was produced in significant amounts which varied linearly with dose. Table 3.13 lists the values of G (acetaldehyde) for various ethylene glycol concentrations.

Table 3.13

Variation of G(acetaldehyde) with ethylene glycol concentration in solutions containing 0.01 M N_2O

<u>[ethylene glycol]</u>	G(acetaldehyde)
0.177 M	1.60
0.876 M	5.80
1.23 M	9.23
1.77 M	8.97

The above data are illustrated in Fig. 8.

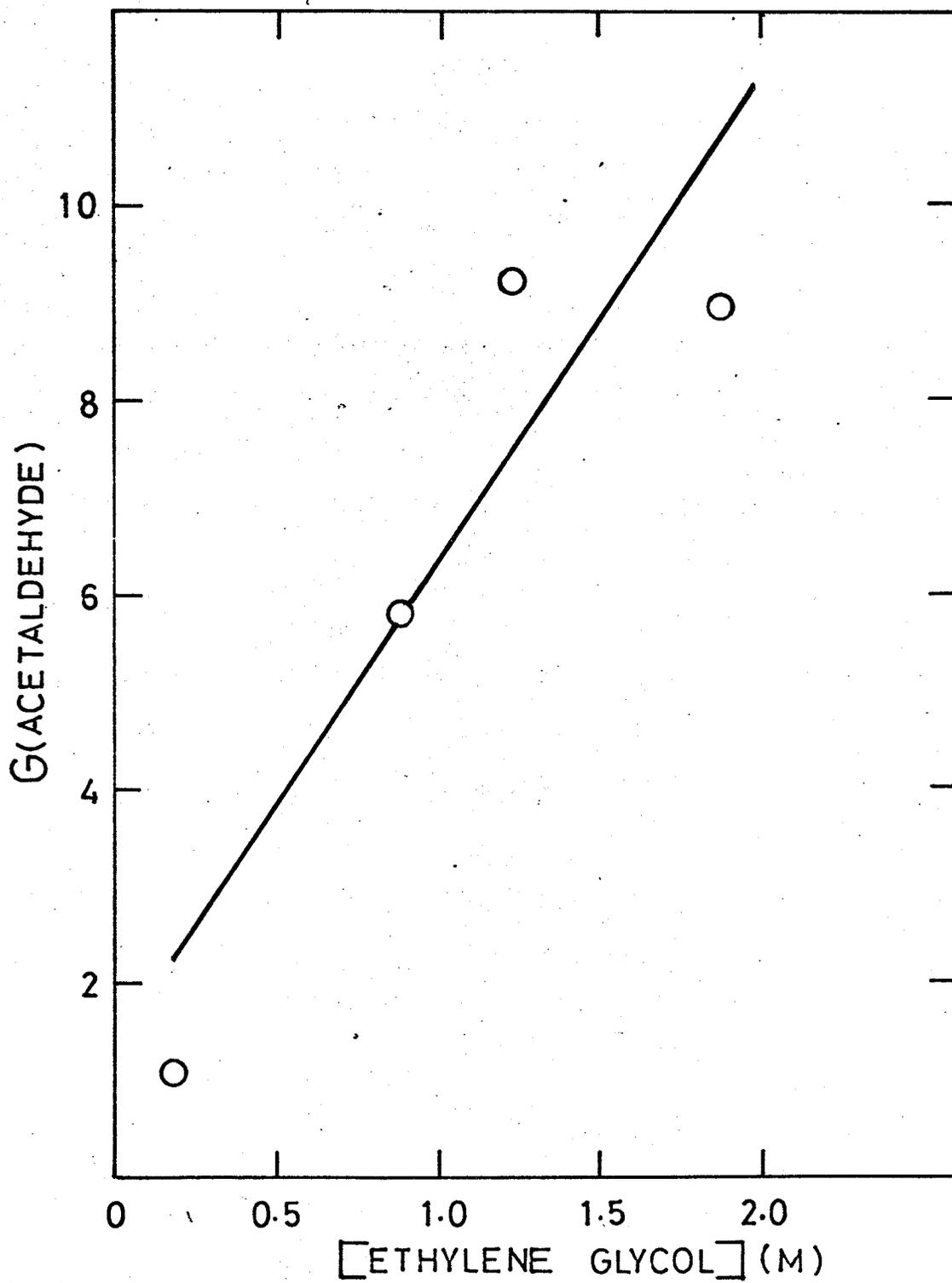
At an ethylene glycol concentration of 1.8 M, G(acetaldehyde) is about 9 which is approximately double the value of 4.3 obtained without any electron scavenger present. Fig. 8 clearly shows a glycol concentration effect which is very nearly linear within experimental error, but the slope of the line is somewhat less than that obtained for the system containing hydrogen peroxide. At 0.05 M ethylene glycol the extrapolated value for G(acetaldehyde) is 1.6 ± 0.8 which agrees within experimental error with the value of 1.3 ± 0.1 obtained by Seidler and v.Sonntag (38) for an ethylene glycol- N_2O solution.

Experiments were also performed to discover whether the system containing N_2O showed any dose

Fig. 8

Variation of G(acetaldehyde) with ethylene glycol concentration. All solutions contained 0.01 M nitrous oxide.

FIG. 8



rate effects. The results of these experiments are found in Table 3.14

Table 3.14

Variation of G(acetaldehyde) with dose rate

<u>[ethylene glycol]</u>	dose rate (eVl ⁻¹ sec ⁻¹)	G(acetaldehyde)
1.77 M	1.42 x 10 ¹⁹	10.2
1.77 M	3.56 x 10 ¹⁸	38.2

The dose rate effects are even larger in this system than in the peroxide system as G(acetaldehyde) increases about 3.8 times when the dose rate is attenuated to one-quarter its normal value.

C. Ethylene Glycol-O₂ in Aqueous Solution

An air-saturated solution along with one more concentrated in oxygen were prepared and irradiated. Neither solution contained hydrogen peroxide or nitrous oxide initially. In both cases hydrogen peroxide was produced during irradiation and its concentration increased to a maximum and then began to fall off. Significant amounts of acetaldehyde were produced only after the peroxide maximum had been reached. Therefore G(acetaldehyde) values were calculated using only the dose absorbed after this time. A larger dose was required to reach the peroxide maximum in the oxygen-rich solution than

in the air-saturated solution. The results observed were, in fact, very similar to those obtained by Van Buskirk (24) for many organic compounds including 2-propanol, t-butyl alcohol, allyl alcohol, and several amines. The usual parameters of the reaction are tabulated in Table 3.14 and the course of a typical reaction is illustrated in Fig. 9. The critical dose refers to the dose required to reach the maximum peroxide concentration.

Table 3.14

Variation of reaction parameters with oxygen concentration. All solutions contained 1.78 M ethylene glycol.

G(acetaldehyde)	$10^4 \times k_{app}$ (sec ⁻¹)	max[H ₂ O ₂]
13.2	1.27	1.0 x 10 ⁻² M
12.8	4.39	1.5 x 10 ⁻⁴ M
17.0	5.26	3.0 x 10 ⁻⁴ M
	initial O ₂	critical dose (eVl ⁻¹)
	degassed	zero
	air-saturated	4.1 x 10 ²¹
	O ₂ -enriched	8.3 x 10 ²¹

It will be noticed that after the critical dose has been absorbed the decay of the peroxide is first order and that k_{app} changes by only 3.4 times while the maximum peroxide concentration changes by 30-60 times. G(acetaldehyde) does not

Fig. 9

Variation of acetaldehyde concentration and hydrogen peroxide concentration with dose in a 1.8 M ethylene glycol/air-saturated solution.

acetaldehyde



hydrogen peroxide



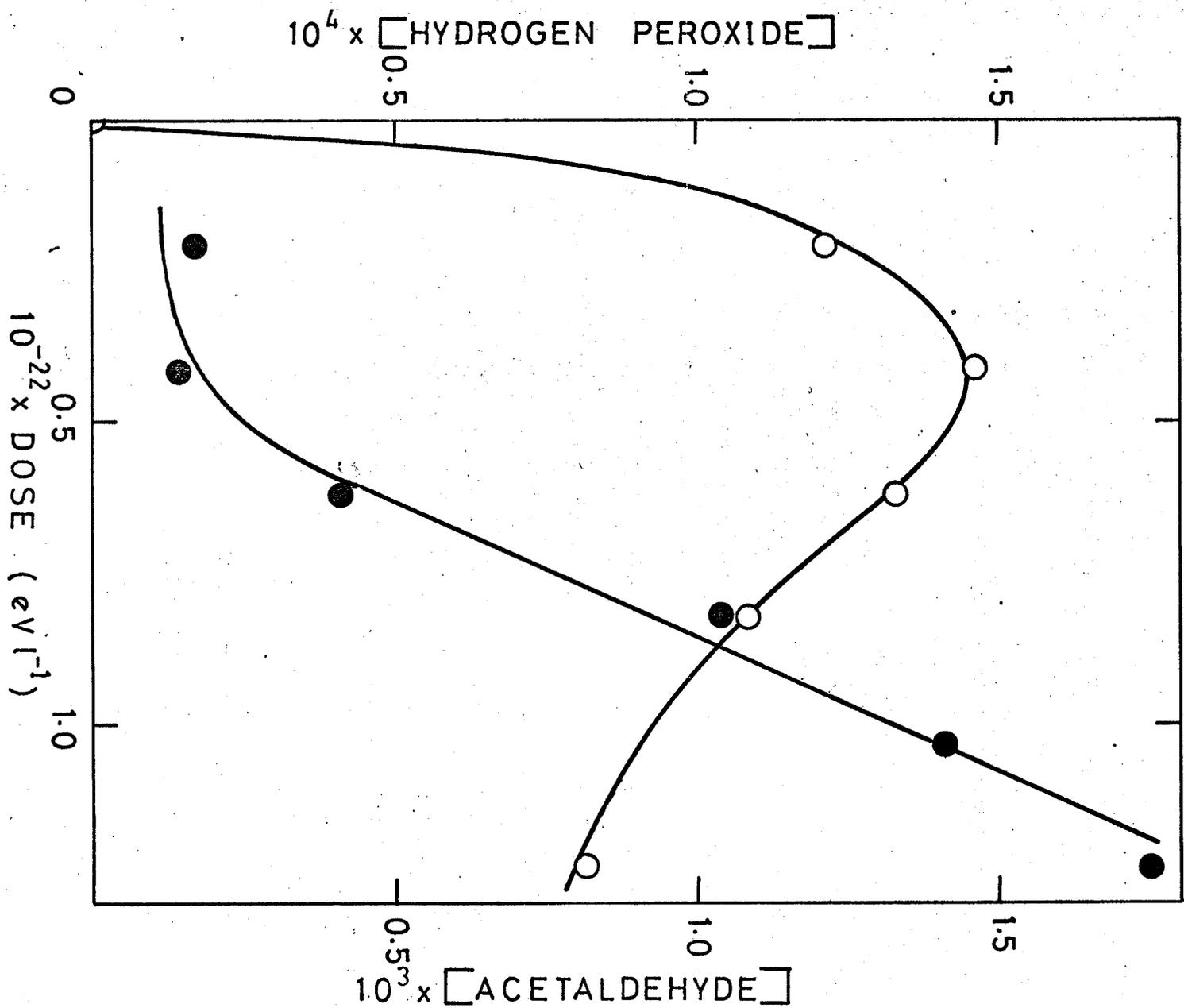


FIG. 9

change very significantly as the initial oxygen concentration varies from zero almost to saturated. In other words, once the peroxide maximum is reached the systems behave in a similar fashion to that of deaerated solutions.

D. Other Glycols in Deaerated Aqueous Solution

3.8 Butane-2,3-diol

An aqueous solution 0.01 M in hydrogen peroxide and containing 1.6 M butane-2,3-diol was degassed and irradiated up to a dose of 5.0×10^{19} eVl⁻¹. Methyl ethyl ketone was produced in concentrations up to 1.5×10^{-3} M. Thus, a reaction analogous to the ethylene glycol one occurs but is apparently less important. Several other peaks were present in the gas chromatogram in addition to the methyl ethyl ketone peak including a very large one with a relatively short retention time (one minute as opposed to about six for methyl ethyl ketone). None of these extra peaks were identified. Although additional peaks were also found in the nitrous oxide system, this latter scavenger was used in all experiments because the dose-yield plots were linear in this case unlike those for the hydrogen peroxide system. G(methyl ethyl ketone)

was measured at several different butane-2,3-diol concentrations and the results are listed in Table 3.15 and shown graphically in Fig. 10.

Table 3.15

Variation of G(methyl ethyl ketone) with butane-2,3-diol concentration. All solutions contained 0.01 M N_2O .

<u>butane-2,3-diol</u>	G(methyl ethyl ketone)
0.108 M	1.01
0.539 M	1.49
1.10 M	1.79
1.64 M	1.95

G(methyl ethyl ketone) is definitely dependent on the glycol concentration but the relationship appears to be more complex than that for ethylene glycol. It is also apparent that the G values for the butane-2,3-diol system are much lower than the corresponding values in the ethylene glycol system.

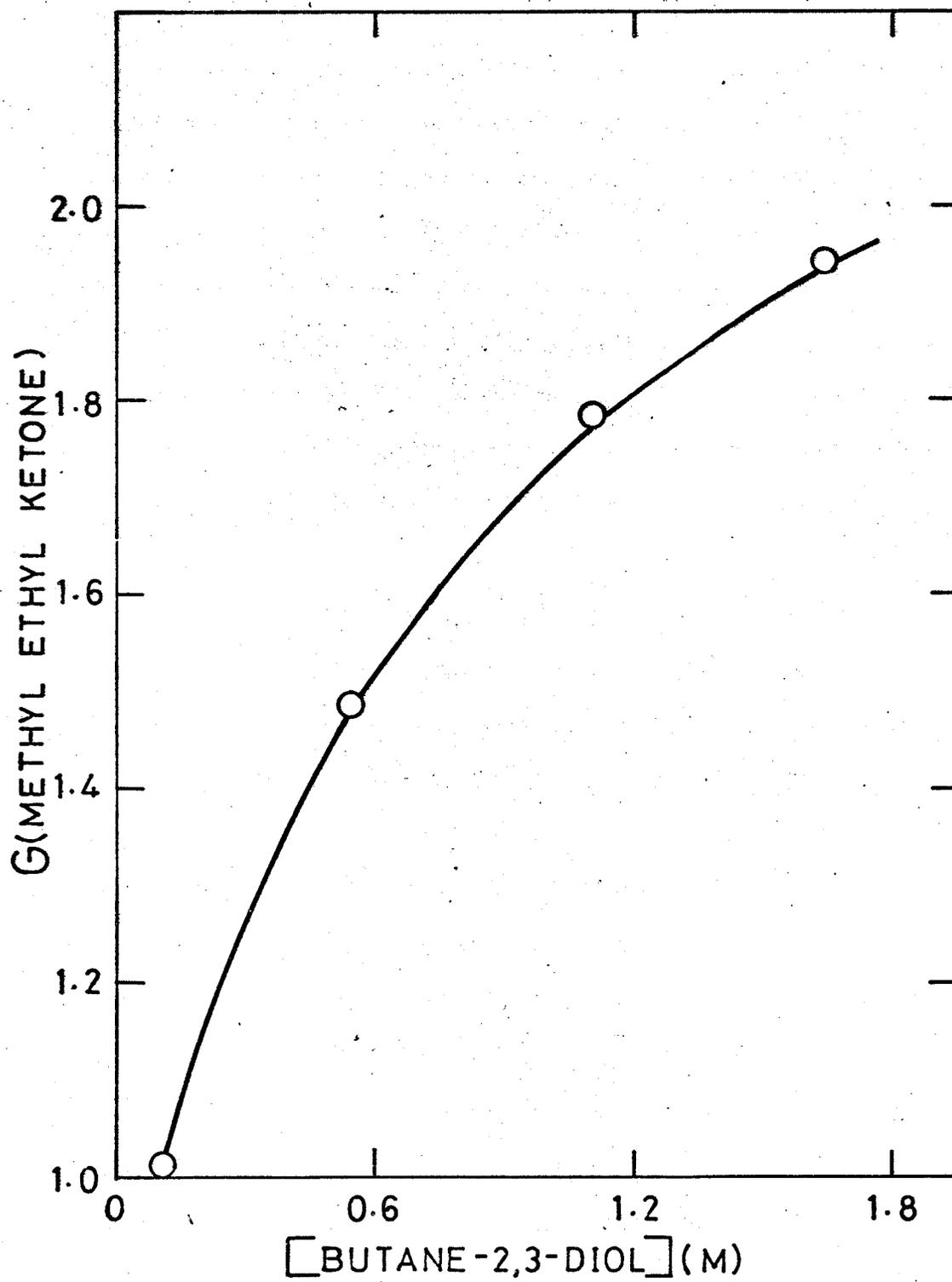
3.9 Propylene Glycol

When a degassed, aqueous solution, 0.01 M in hydrogen peroxide and 1.34 M in propylene glycol, was irradiated significant amounts of acetone were produced. A dose of $4.9 \times 10^{19} \text{ eV l}^{-1}$ resulted in a concentration of $1.67 \times 10^{-2} \text{ M}$ acetone, an amount

Fig. 10

Variation of G(methyl ethyl ketone) with butane-
2,3-diol concentration. All solutions were
0.01 M in N_2O .

FIG. 10



of product greater than that formed in ethylene glycol solutions under similar conditions. Both the peroxide and nitrous oxide systems yielded results that were too complex to obtain accurate G values. The gas chromatogram consisted of a number of peaks none of which were identified. However, in the one solution examined, the disappearance of peroxide was clearly first order in peroxide. The solution 0.01 M in hydrogen peroxide and 1.34 M in propylene glycol had an apparent rate constant for peroxide destruction of $0.809 \times 10^{-4} \text{ sec}^{-1}$.

3.10 Summary

As far as the investigation went, the chain formation of an aldehyde or ketone under irradiation appeared to be a general one for glycols. Both the butane 2,3 diol and the propylene glycol systems displayed certain features in common with the ethylene glycol system. In the case of the butane 2,3 diol-N₂O system, methyl ethyl ketone was produced linearly with dose, and G(methyl ethyl ketone) was dependent upon the glycol concentration. The peroxide removal in the propylene glycol-H₂O₂ solutions was first order in peroxide. On the whole, however, these two systems appeared to be much more complex than the ethylene glycol system.

4. Discussion

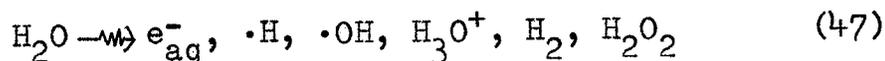
A. Ethylene Glycol-H₂O₂ in Deaerated Aqueous Solution

4.1 Acetaldehyde Formation

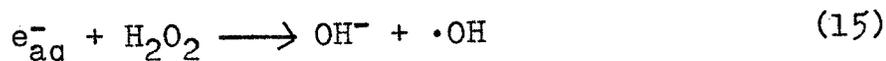
The significant characteristics of the reaction which produces acetaldehyde upon γ -irradiation of deaerated aqueous ethylene glycol-H₂O₂ solutions are:

- (a) it is a chain reaction
- (b) G(acetaldehyde) is linearly dependent upon the glycol concentration.
- (c) the reaction is catalyzed by hydrogen peroxide but after a concentration of less than 10^{-4} M peroxide is attained, G(acetaldehyde) is essentially independent of the peroxide concentration.

The following mechanism is proposed to explain the observed results. At the solute concentrations used the γ -radiation can be considered to react almost exclusively with the bulk solvent, water.

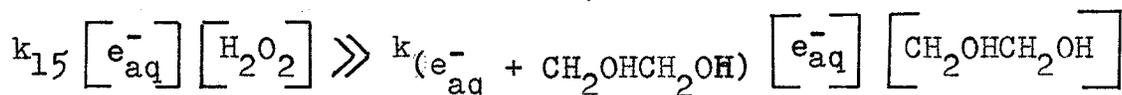


The hydrated electrons react with the hydrogen peroxide to produce $\cdot\text{OH}$ radicals.



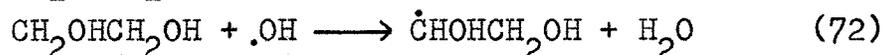
Although no value could be found for the rate constant of the reaction between hydrated electrons

and ethylene glycol, it is not unreasonable to assume that its value is similar to that for reactions between hydrated electrons and other alcohols such as methanol and ethanol. Thus,



and reaction (15) is the only one for the hydrated electrons (40).

The chain reaction is then initiated by the attack of $\cdot H$ and $\cdot OH$ radicals on the ethylene glycol molecules via hydrogen atom abstraction.



The reaction between hydrogen peroxide and $\cdot H$ and $\cdot OH$ respectively need not be considered because:

$$k_{71} [\cdot H] [CH_2OHCH_2OH] \cong 16 k_{(\cdot H + H_2O_2)} [\cdot H] [H_2O_2]$$

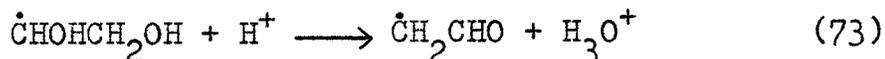
and

$$k_{72} [\cdot OH] [CH_2OHCH_2OH] \gg k_{14} [\cdot OH] [H_2O_2] \quad (40)$$

Evidence for the formation of the radical $\dot{C}HOHCH_2OH$ is provided by e.s.r. data. Upon photolyzing 1% H_2O_2 in ethylene glycol, Livingston and Zeldes (41) obtained the spectrum of this radical. The addition of water simply made the spectra progressively weaker.

The radical $\dot{C}HOHCH_2OH$ can either rearrange or

eliminate a water molecule to form $\dot{\text{C}}\text{H}_2\text{CHO}$ which is the immediate precursor of acetaldehyde. It is believed that this transformation is acid catalyzed and therefore can be written:



Livingston and Zeldes (42) have obtained evidence for the above reaction. As mentioned before when these authors photolyzed a small amount of H_2O_2 in ethylene glycol they obtained a spectrum of 24 sharp lines arising from $\dot{\text{C}}\text{HOHCH}_2\text{OH}$. They later found some very weak lines which grew in intensity upon adding small amounts of acid. When they added 0.5 ml. of concentrated HCl/1. to a 50:50 water and ethylene glycol solution the spectrum changed into a broad triplet. Livingston and Zeldes present conclusive evidence that the spectrum is not due to $\dot{\text{C}}\text{H}_2\text{OH}$ formed from C-C bond cleavage and they also offer reasonable arguments against a ring structure such as $\text{CH}_2 \begin{array}{c} \diagup \text{O} \diagdown \\ \text{---} \end{array} \dot{\text{C}}\text{H}$.

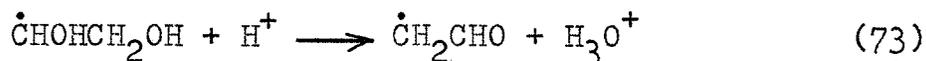
It has been determined that at 24.0°C the fraction of acetaldehyde molecules hydrated is .553 (43). If about 50% of the acetaldehyde itself is present as the hydrate then the radical $\dot{\text{C}}\text{H}_2\text{CHO}$ which is similar may exist as the hydrate $\dot{\text{C}}\text{H}_2\text{CH}(\text{OH})_2$ and thus reac-

tion (73) may be a rearrangement rather than an elimination.

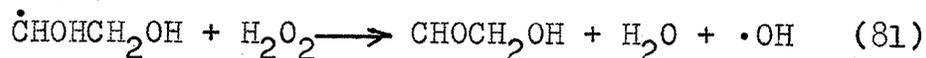
In the event of an elimination Seidler and Sonntag (38) have shown that the hydrogen atom and hydroxyl radical eliminated must originate from the OH groups on the parent glycol radical. The elimination suggested by Seidler and Sonntag would result in the formation of the radical $\text{HCO}\dot{\text{C}}\text{H}_2$. The $p\pi$ -interaction between the unpaired electron and the carbonyl group should stabilize the radical.



The work of Livingston and Zeldes suggests that the reaction, whether a rearrangement or an elimination, is acid catalyzed. For convenience sake, reaction (73) will be referred to as a rearrangement.

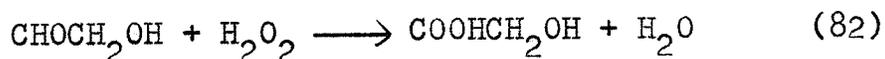


It is now suggested that this rearrangement step occurs in competition with the oxidation of $\dot{\text{C}}\text{HOHCH}_2\text{OH}$ by the hydrogen peroxide.

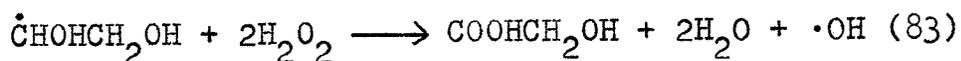


This oxidative chain propagation step is followed by a stoichiometric thermal oxidation of the glycolaldehyde to glycolic acid which has been detected as a

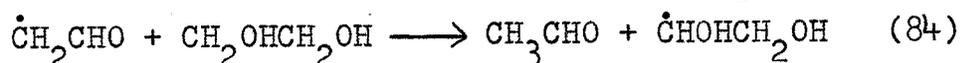
final product.



Reactions (81) and (82) are summarized in equation (83).



The rearranged radical, $\dot{\text{C}}\text{H}_2\text{CHO}$, once formed reacts with ethylene glycol to abstract a hydrogen atom to form acetaldehyde and the $\dot{\text{C}}\text{HOHCH}_2\text{OH}$ radical.



This radical conversion reaction is partly suggested by the experimental results. The dependence of $G(\text{acetaldehyde})$ on glycol concentration could be rationalized by assuming a competition between a chain termination step involving the rearranged radical and reaction (84). One can also find support for this type of reaction in the literature. Thomas (44) has observed the reaction of methyl radicals with 2-propanol in which the methyl radical presumably abstracts a hydrogen atom to form methane and an α -alcohol radical. The radical $\dot{\text{C}}\text{H}_2\text{CHO}$ can be considered a substituted methyl radical and should likewise be able to abstract an α -hydrogen from an alcohol. Due to the increased degree of ordering in the transition state the rate constant for reaction (84) could be expected to be somewhat lower

than $3.4 \times 10^3 \text{M}^{-1} \text{sec}^{-1}$ measured by Thomas for the methyl radical 2-propanol reaction.

Norman and West (16) have suggested a radical conversion reaction to explain the variation in intensity of e.s.r. spectra as the substrate concentration is changed in the metal-ion catalyzed reaction of organic compounds with hydrogen peroxide.

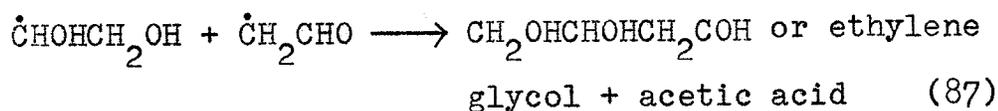
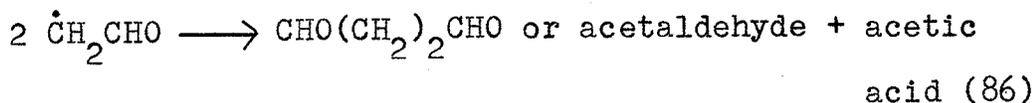
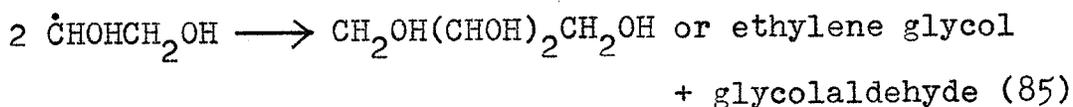
A radical conversion reaction could also be used to explain some of the results of Livingston and Zeldes (41) mentioned earlier. They observed that the e.s.r. spectrum of $\dot{\text{C}}\text{HOHCH}_2\text{OH}$ became progressively weaker as water was added to the system. When the system has a high ethylene glycol concentration a large proportion of the $\dot{\text{C}}\text{HOHCH}_2\text{OH}$ radicals could be formed from the rearranged radicals by reaction (84) but as the concentration of glycol is reduced the rate of reaction (84) decreases. The growth of the $\dot{\text{C}}\text{H}_2\text{CHO}$ spectrum might not be detected due to the broadness of the peaks but the decrease in size of the sharp lines of the $\dot{\text{C}}\text{HOHCH}_2\text{OH}$ spectrum would be observed.

Burchill and Ginns (26) have proposed such a reaction to explain the alcohol concentration dependence shown in the radiation-induced oxidation of

2-propanol by hydrogen peroxide. These authors suggest that the β -radical of 2-propanol, $\text{CH}_3\text{CHOH}\dot{\text{C}}\text{H}_2$, can abstract a hydrogen atom from 2-propanol to produce the α -radical $(\text{CH}_3)_2\dot{\text{C}}\text{OH}$. They also present evidence that an analogous reaction takes place for ethanol. These reactions are very similar to that presented in equation (84).

Finally, two radicals must either disproportionate or combine in a chain termination step.

Three different bimolecular terminations are possible:

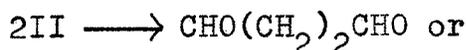
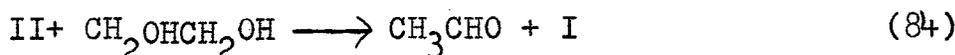
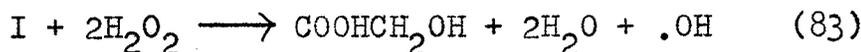
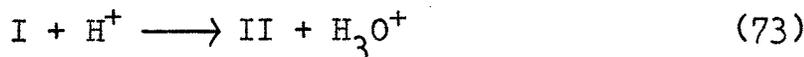
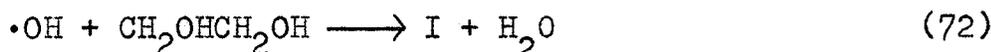
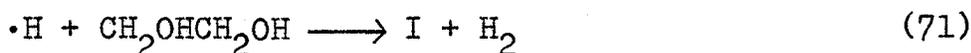
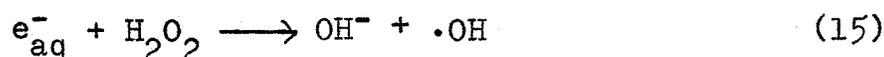
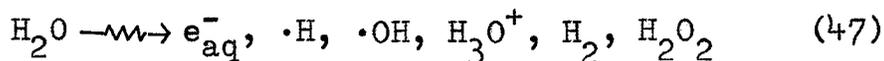


The relatively large concentration of glycol and peroxide in the system, the low steady-state concentration of the primary radicals and their high rate of reaction with glycol and peroxide make it unlikely that $\cdot\text{H}$, $\cdot\text{OH}$, or e_{aq}^- play any role in the chain termination.

As none of the termination products were determined nothing very conclusive can be said about the

relative rates of the three proposed termination reactions. Although all three could take place to some extent, evidence is offered later for considering reaction (86) as most probable and so, for convenience, it will be the only termination reaction considered in the summary that follows.

The proposed mechanism is as follows:



acetaldehyde + acetic acid (86)

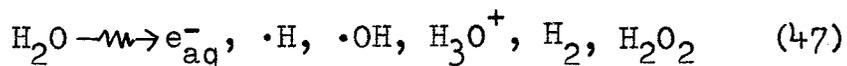
I represents $\dot{C}HOHCH_2OH$ and II represents $\dot{C}H_2CHO$.

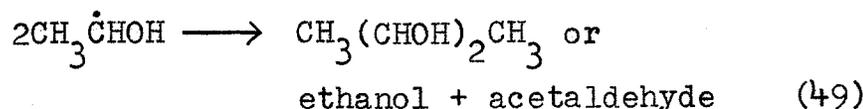
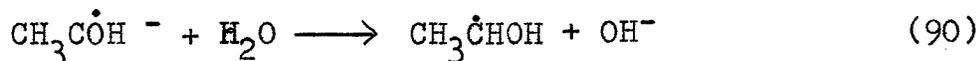
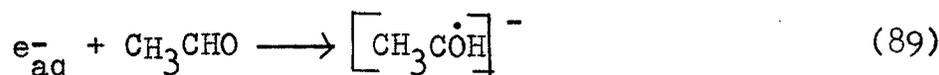
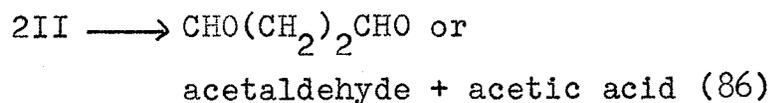
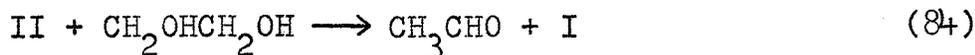
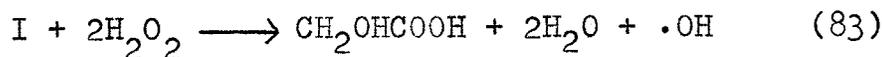
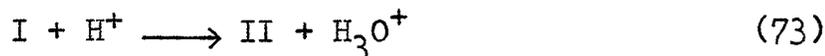
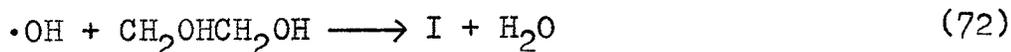
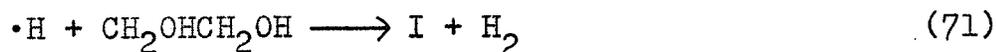
Using normal steady-state approximations an expression for G(acetaldehyde) can be obtained for the proposed mechanism.

$$G(\text{acetaldehyde}) = k_{34} \sqrt{\frac{G_{e_{aq}^-} + G_H + G_{OH}}{2k_{86}D}} [\text{glycol}] + \frac{G_{e_{aq}^-} + G_H + G_{OH}}{2} \quad (88)$$

D is the dose rate in units of $6.02 \times 10^{25} \text{ eV l}^{-1} \text{ sec}^{-1}$ and $[\text{glycol}]$ is the concentration of ethylene glycol in moles l^{-1} . Several features of the mechanism are immediately apparent from an examination of equation (88). G(acetaldehyde) should be linearly dependent upon ethylene glycol concentration as was found to be the case. Equation (88) also predicts that G(acetaldehyde) will be independent of the hydrogen peroxide concentration. Except at extremely low peroxide concentration this prediction agrees with the experimental results.

In order to explain the situation at low peroxide concentration the statement made earlier that reaction (15) is the only one for hydrated electrons must be re-examined. When the hydrogen peroxide concentration approaches zero, reaction (15) will eventually fail to convert all the hydrated electrons into $\cdot\text{OH}$ radicals. At zero initial peroxide concentration only that H_2O_2 produced by the interaction of the radiation with the water will be available for reaction. Under these conditions the mechanism involved is believed to be as follows:





I represents the radical $\dot{\text{C}}\text{HOHCH}_2\text{OH}$ and II represents $\dot{\text{C}}\text{H}_2\text{CHO}$. As the only source of peroxide is reaction (47) only a very minute amount of peroxide, the steady-state concentration, is available for reaction. Since the concentration of acetaldehyde is ever increasing and since $k_{15} \cong k_{89}$ (40) the hydrated electrons will probably react solely with the acetaldehyde except very early in the reaction. Because $k_9 \cong k_{89}$ the reaction between two hydrated electrons to produce H_2 will likewise only be important very early in the reaction when the concentration of acetaldehyde is not large.

Reaction (90) occurs because the pK value for $[\text{CH}_3\text{C}\dot{\text{O}}\text{H}]^-$ is 11.6 (39). The termination steps, reactions (86) and (49) are only two possibilities but some such reactions involving the radicals $\dot{\text{C}}\text{H}_2\text{CHO}$ and $\text{CH}_3\dot{\text{C}}\text{HOH}$ probably take place to terminate the chain.

Although a yield expression was not derived for G(acetaldehyde) from this mechanism several arguments can be offered to show that the experimental value of 4.3 is reasonable. Hydrated electrons are not being converted to $\cdot\text{OH}$ radicals and this lowers the concentration of I and ultimately of II. This effect alone may lower G(acetaldehyde) to about two-thirds of its value of 13.2 in a peroxide system, the exact fraction depending upon which terminating reactions are occurring and to what extent. Also, the acetaldehyde produced is being destroyed by the hydrated electrons. This reaction may lower the value of G(acetaldehyde) by as much as 2.5 molecules/100 eV or more.

To return to the original mechanism dealing with systems containing hydrogen peroxide initially, equation (88) was derived on the assumption that acetaldehyde was formed in the termination reaction.

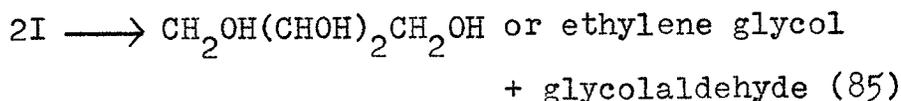
$$G(\text{acetaldehyde}) = k_{84} \sqrt{\frac{G_{e_{ag}^-} + G_H + G_{OH}}{2k_{86}D}} [\text{glycol}] + \frac{G_{e_{ag}^-} + G_H + G_{OH}}{2} \quad (88)$$

If this assumption is correct $G^0(\text{acetaldehyde})$, the value obtained by extrapolation to zero $[\text{glycol}]$ should equal $\frac{G_{e_{ag}^-} + G_H + G_{OH}}{2}$ or 2.8. If acetaldehyde is not formed as a termination product then $G^0(\text{acetaldehyde})$ should equal zero. The measured intercept, 0.10, suggests that the latter situation is predominant and thus the following equations can be written in place of reactions (86) and (88).



$$G(\text{acetaldehyde}) = k_{84} \sqrt{\frac{G_{e_{ag}^-} + G_H + G_{OH}}{2k_{86}D}} [\text{glycol}] \quad (88a)$$

When reaction (85) is considered in place of reaction (86) as a termination step the yield expression changes somewhat.



Regardless of whether reaction (85) is considered as a disproportionation or as a biradical combination the analytical expression obtained is as follows:

$$G(\text{acetaldehyde}) = k_{84} \sqrt{\frac{G_{e^-} + G_H + G_{OH}}{2k_{85}D}} \quad (91)$$

In this case $G(\text{acetaldehyde})$ would show no ethylene glycol dependence and therefore reaction (85) is not very significant if it occurs at all.

4.2 Hydrogen Peroxide Destruction

The significant characteristics of the oxidative chain reaction are as follows:

- (a) the peroxide removal is first order in hydrogen peroxide.
- (b) the apparent rate constant for peroxide destruction, k_{app} , is linearly dependent on the ethylene glycol concentration in the range .18 M to 1.8 M.
- (c) the magnitude of k_{app} is essentially independent of the hydrogen peroxide concentration in the region examined.

An expression was obtained from the proposed mechanism for the rate of disappearance of hydrogen peroxide in systems containing peroxide initially.

$$\begin{aligned}
 -\frac{d}{dt} [\overline{\text{H}_2\text{O}_2}] &= (G_{e_{\text{aq}}^-} - G_{\text{H}_2\text{O}_2})D \\
 &+ \frac{k_{83}}{k_{73}[\text{H}^+]} \left[\frac{k_{84} \sqrt{\frac{(G_{e_{\text{aq}}^-} + G_{\text{H}} + G_{\text{OH}})D}{2k_{86}}} [\text{glycol}]}{+ (G_{e_{\text{aq}}^-} + G_{\text{H}} + G_{\text{OH}})D} \right] [\overline{\text{H}_2\text{O}_2}] \quad (92)
 \end{aligned}$$

If one neglects the first term on the right hand side of equation (92) the expression can be integrated to yield equation (93).

$$\begin{aligned}
 -\ln [\overline{\text{H}_2\text{O}_2}] &= \frac{k_{83}}{k_{73}[\text{H}^+]} \left[\frac{k_{84} \sqrt{\frac{(G_{e_{\text{aq}}^-} + G_{\text{H}} + G_{\text{OH}})D}{2k_{86}}} [\text{glycol}]}{+ (G_{e_{\text{aq}}^-} + G_{\text{H}} + G_{\text{OH}})D} \right] t \quad (93)
 \end{aligned}$$

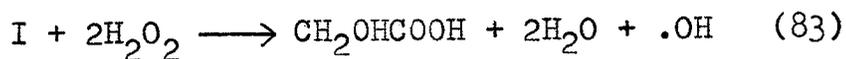
Equation (93) predicts a decay of hydrogen peroxide that is first order in peroxide and therefore agrees with the observed results. An expression for the apparent rate constant for this reaction can be derived from equation (93).

$$\begin{aligned}
 k_{\text{app}} &= \frac{k_{83}}{k_{73}[\text{H}^+]} \left[\frac{k_{84} \sqrt{\frac{(G_{e_{\text{aq}}^-} + G_{\text{H}} + G_{\text{OH}})D}{2k_{86}}} [\text{glycol}]}{+ (G_{e_{\text{aq}}^-} + G_{\text{H}} + G_{\text{OH}})D} \right] \quad (94)
 \end{aligned}$$

According to equation (94) the proposed mechanism implies that k_{app} will be linearly dependent upon the glycol concentration and independent of the peroxide concentration, all as observed experimentally. It may be noted that if reaction (85), the reaction of two type I radicals, were the terminating step then k_{app} would be independent of glycol concentration contrary to the observed results.

4.3 The Oxidation Product

In Fig. 11 the relationship between hydrogen peroxide destruction and glycolic acid production is illustrated. Although the relationship is not a stoichiometric one, Fig. 11 demonstrates that reaction (83) probably takes place along with other complicating oxidation reactions.



Some of radical I may end up oxidized to oxalic acid or even carbon dioxide.

Vasudeva and Wasif (45) have investigated the thermal free radical oxidation of ethylene glycol by peroxydisulfate. These authors suggest that the peroxydisulfate, upon being heated, produces sulfate radicals which react with water to form hydroxyl radicals. The glycol radicals $\dot{C}HOHCH_2OH$

Fig. 11

Variation of glycolic acid concentration and hydrogen peroxide concentration with irradiation time at a dose rate of 1.43×10^{19} $\text{eVl}^{-1}\text{sec}^{-1}$.

glycolic acid ●

hydrogen peroxide ○

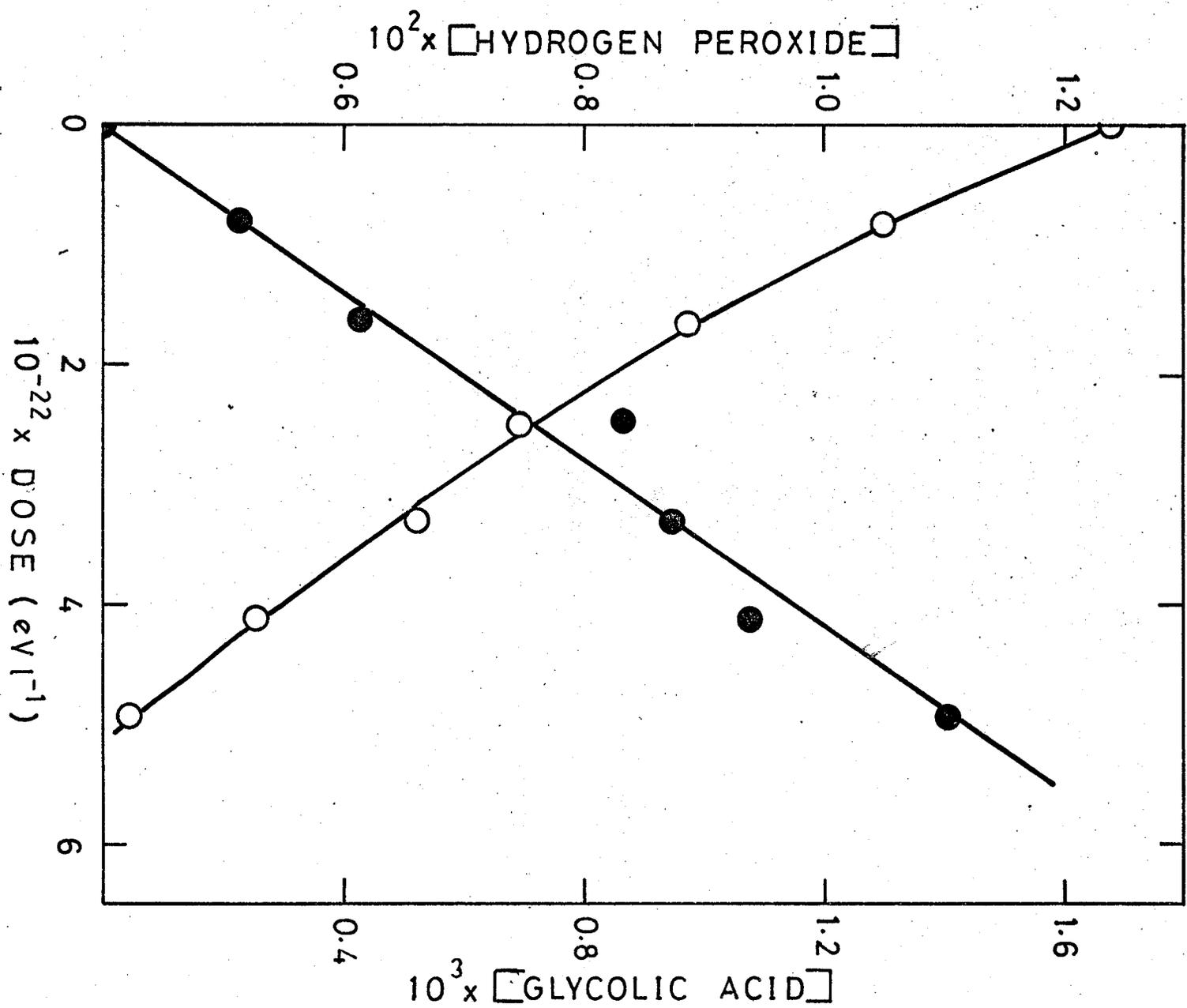


FIG. 11

subsequently produced by hydrogen atom abstraction are then oxidized by the sulfate radicals and the peroxydisulfate to form glycolaldehyde. It should be noted that no glycolaldehyde was reported as a reaction product but that glycolic acid and oxalic acid were found and attributed to the oxidation of glycolaldehyde. The specific methods used to identify these products were not given and it is possible that acetaldehyde was formed by a rearrangement process similar to that proposed in this work but was not detected.

4.4 Summary

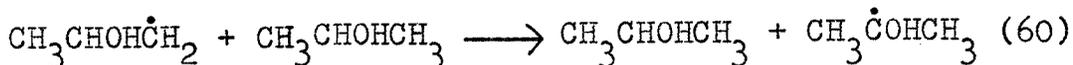
In summary, all the significant features of the reaction - the dependence of $G(\text{acetaldehyde})$ and k_{app} upon glycol concentration, the independence of the rearrangement chain from the oxidative chain, the first order destruction of hydrogen peroxide, and the low sensitivity of k_{app} to changes in initial peroxide concentration - are predicted by the analytical expressions derived from the proposed mechanism. The lowering of $G(\text{acetaldehyde})$ when peroxide is omitted from the system can be explained by including the established reaction of acetaldehyde with hydrated electrons.

From equations (88) and (94) values may be obtained for k_{84} , the rate constant for the conversion of radical II to radical I, and k_{73} , the rate constant for the rearrangement step. When $G(\text{acetaldehyde})$ is plotted against ethylene glycol concentration a straight line results whose slope is equal to

$$k_{84} \sqrt{\frac{G_{e_{aq}^-} + G_H + G_{OH}}{2k_{86}D}}$$

A value for k_{84} may be obtained by equating this expression to the measured slope if values are assumed for the remaining constants. D is the measured dose rate in units of $6.02 \times 10^{25} \text{ eVl}^{-1}\text{sec}^{-1}$ and its value is 2.33×10^{-7} . The primary radical yields, $G_{e_{aq}^-}$, G_H , and G_{OH} , are reasonably well established (12), (13) and values of 2.58, 0.6, and 2.72 respectively will be used here. There is no recorded value for k_{86} , the rate constant for the termination step, but $1.2 \times 10^9 \text{ M}^{-1}\text{sec}^{-1}$ has been obtained for both methanol and ethanol radical combinations. It is reasonable to assume that k_{86} is of the same order of magnitude. Substitution leads to $\frac{k_{84}}{2k_{86}} = 1.52 \times 10^{-3} \text{ M}^{-\frac{1}{2}}\text{sec}^{-\frac{1}{2}}$ and $k_{84} = 75 \text{ M}^{-1}\text{sec}^{-1}$. The latter figure is comparable to the value of $53 \pm 10 \text{ M}^{-1}\text{sec}^{-1}$ (26) obtained by Burchill and Ginns for the analogous

radical conversion reaction:



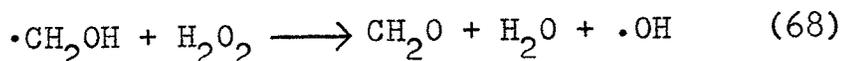
When the apparent rate constant for peroxide removal, k_{app} , is plotted against glycol concentration the resulting straight line has a slope equal to

$$\frac{k_{83}}{k_{73}[\text{H}^+]} \left[\frac{k_{84}}{2.30} \sqrt{\frac{(G_{e^-} + G_{\text{H}} + G_{\text{OH}})D}{2k_{86}}} \right]$$

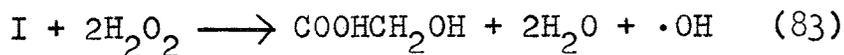
By equating this expression to the measured slope and substituting the values of D and of the primary yields listed previously, and the value of $\frac{k_{84}}{\sqrt{2k_{86}}}$ obtained experimentally one finds that

$$\frac{k_{73}}{k_{83}} [\text{H}^+] = 2.48 \times 10^2 .$$

Although no value for k_{83} could be found in the literature, it was discovered that Burchill and Ginns (27) had obtained a value of $4.0 \times 10^4 \text{ M}^{-1}\text{sec}^{-1}$ for k_{68} , the rate constant for the reaction between a methanol radical and hydrogen peroxide.



Because reaction (68) is quite similar to reaction (83) it is not unreasonable to assume that their rate constants will be of the same order of magnitude.

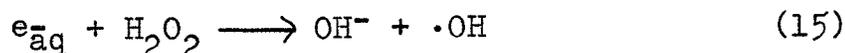
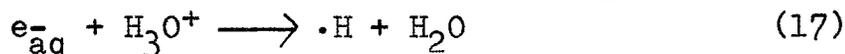
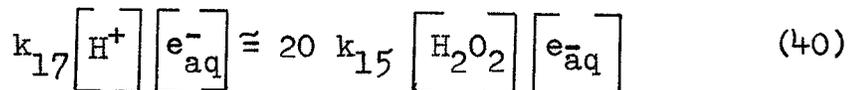


Using the value of k_{68} for k_{83} one finds that the rate constant for the rearrangement reaction, k_{73} , equals $9.9 \times 10^2 [H^+] M^{-1}sec^{-1}$

4.5 pH Effects

G(acetaldehyde) was found to be independent of pH within experimental error in the pH range 1-6. However, as the pH was raised to 9.2 a considerable increase in G(acetaldehyde) was noted.

At low pH the hydrated electrons are believed to react mainly with the hydrogen ions as described in equation (17) because



The $\cdot H$ atoms produced in reaction (17) abstract hydrogen atoms from ethylene glycol in a similar manner to $\cdot OH$ radicals produced by reaction (15).

The net result should be that G(acetaldehyde) remains constant as the pH is changed which agrees with the observed results. The increase noticed at pH 9.2 cannot be explained at this time. When Livingston and Zeldes (42) titrated an aqueous solution of ethylene glycol containing 1% H_2O_2 from a pH of

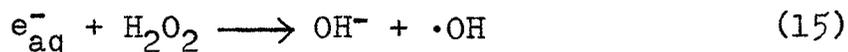
about 5 upwards they observed that at pH 9.3 the e.s.r. spectrum of $\dot{\text{C}}\text{HOHCH}_2\text{OH}$ disappeared and in its place were several broad lines of unknown origin. It is entirely possible that around this pH value a somewhat different mechanism is in operation. More experimental work must be done before any hypothesis can be formed concerning the nature of this mechanism.

If we consider reaction (17) the only reaction involving hydrated electrons at low pH and reaction (15) their only reaction in neutral solution then analytical expressions for $-d[\text{H}_2\text{O}_2]/dt$ can be derived in both instances. Although the expressions are slightly different, after suitable approximations have been made in order that the expressions may be integrated both turn out to be identical. Thus equation (93) should apply throughout the entire pH range 1 to 6 and possibly higher.

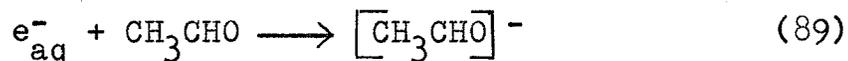
$$-\ln [\text{H}_2\text{O}_2] = \frac{k_{83}}{k_{73}[\text{H}^+]} \left[\frac{k_{84} \sqrt{(G_{e^-} + G_{\text{H}} + G_{\text{OH}})D}}{2k_{86}} [\text{glycol}] + (G_{e^-} + G_{\text{H}} + G_{\text{OH}})D \right] t \quad (93)$$

Equation (93) predicts that k_{app} will vary approximately inversely as the hydrogen ion concentration which agrees well with the experimental results.

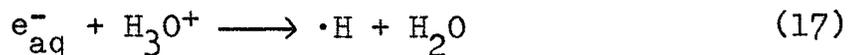
When no hydrogen peroxide was present in the system G(acetaldehyde) increased from 4.3 at pH 6 to 16.1 at pH 1. Without peroxide present the hydrated electrons are not converted to $\cdot\text{OH}$ radicals by reaction (15) and so the concentration of radical I is lowered and the rate of the rearrangement decreases.



Instead, the hydrated electrons will most likely attack the acetaldehyde as described in reaction (89).



For both reasons G(acetaldehyde) is decreased from its value with peroxide in the system. With acid present in concentrations of about 0.1 M reaction (17) will occur and the hydrogen ions will scavenge the electrons to produce $\cdot\text{H}$ atoms thereby increasing the acetaldehyde yield.



The G(acetaldehyde) value attained with acid scavenging the hydrated electrons, 16.1, is comparable to that obtained when peroxide is used as a scavenger, 13.2.

4.6 Dose Rate Effects

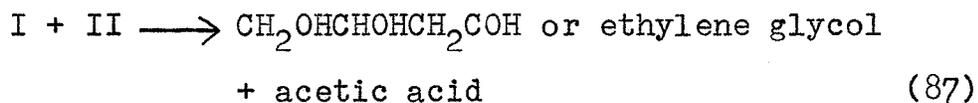
In the system containing peroxide initially G(acetaldehyde) increased by a factor of 2.9 times when the dose rate was attenuated to one-quarter its normal value. This effect is much larger than one would expect on the basis of equation (88a) which predicts that G(acetaldehyde) is inversely proportional to the square root of the dose rate.

According to equation (88a)

$$G(\text{acetaldehyde}) = k_{84} \sqrt{\frac{G_{e-} + G_H + G_{OH}}{2k_{86}D}} \quad [\text{glycol}] \quad (88a)$$

G(acetaldehyde) should only double its value under one-quarter the dose rate.

In an attempt to rationalize this anomalously large dose rate effect several possible explanations were considered but none were found to be completely satisfactory. If reaction (87) is substituted for reaction (86) as the termination step in the proposed mechanism the yield expression changes markedly.



$$G(\text{acetaldehyde}) = \frac{k_{84} G_R}{2k_{87}} [\text{glycol}] \left[\frac{G_R D}{4k_{73} [\text{H}^+]} + \sqrt{\left(\frac{G_R D}{4k_{73} [\text{H}^+]} \right)^2 + \frac{k_{84} G_R D [\text{glycol}]}{2k_{73} k_{87} [\text{H}^+]}} \right]^{-1} \quad (95)$$

$$G_R = G_{e_{\text{aq}}}^- + G_H + G_{\text{OH}}$$

In equation (95) two of the three terms within the bracket predict that the yield simply varies inversely as the dose rate. However, if cross-termination were responsible for the anomalous dose rate effect one would expect the effect to be reduced when the solutions were acidified. At low pH the rearrangement occurs faster and the concentration of $\dot{\text{C}}\text{H}_2\text{CHO}$ is increased thus favoring reaction (86a) as the termination step.



At pH I the dose rate effect was even more pronounced than at pH 6. It might be added at this time that since equation (95) predicts a non-linear relationship between the acetaldehyde yield and the glycol concentration, reaction (87) probably does not play a very significant role in the chain termination.

Other possible explanations for the large dose rate effects that were considered were a

branching chain reaction and a reaction between hydrated electrons and acetaldehyde. However, in both these cases the dose rate effect should be equally marked at moderate and at high dose rates. In the next section it will be shown that at moderate dose rates the yield approaches that predicted by equation (88a).

Considering the peroxide destruction, equation (93) is sufficient to rationalize the dose rate effect upon the apparent rate constant, k_{app} .

$$-\ln \left[\frac{H_2O_2}{2} \right] = \frac{k_{83}}{k_{73} [H^+]} \left[\frac{k_{84} \sqrt{(G_{e_{aq}}^- + G_H + G_{OH}) D}}{2k_{86}} \right] \left[\text{glycol} \right] + (G_{e_{aq}}^- + G_H + G_{OH}) D t \quad (93)$$

Regardless of the exact termination products, k_{app} is dependent upon two terms one of which varies directly as \sqrt{D} while the other varies directly as D . A dose rate dependence somewhat greater than square root is thus expected in the case of k_{app} .

In order to complete the discussion of cross-termination it should be noted that the substitution of reaction (87) for reaction (86) in the proposed mechanism leads to the following expression for k_{app} :

$$k_{app} = k_{83} \left[\frac{G_{RD}}{4k_{73}[H^+]} + \sqrt{\left(\frac{G_{RD}}{4k_{73}[H^+]} \right)^2 + \frac{k_{84} G_{RD} [\text{glycol}]}{2k_{73} k_{87} [H^+]}} \right] \quad (96)$$

Equation (96) provides further evidence that cross-termination is not very significant because it predicts that the very strongest glycol concentration dependence k_{app} could possibly have would be square root contrary to observations.

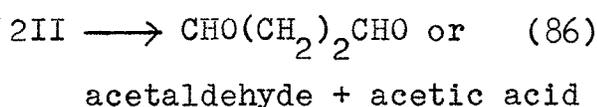
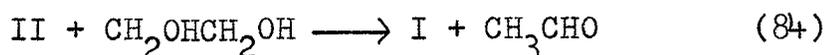
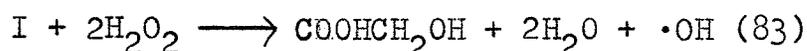
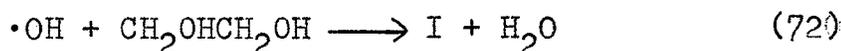
4.7 Photochemical Initiation

The rearrangement was found to occur under UV irradiation with even longer chain lengths than under γ -irradiation as was discussed in the previous chapter. The value of $\Phi(\text{acetaldehyde})$ did not change significantly when the system was acidified to pH 1.

The hydrogen peroxide interacts with the incident photons of UV radiation and thereby decomposes as summarized in equation (43).



The remaining steps are just those expected on the basis of the mechanism proposed for γ -irradiated systems.



The expression for (acetaldehyde) derived for the proposed mechanism is:

$$\Phi(\text{acetaldehyde}) = k_{84} \sqrt{\frac{\Phi_{\text{OH}}}{I_a^{2k_{86}}} [\text{glycol}]} \quad (97)$$

Φ_{OH} is the primary $\cdot\text{OH}$ radical yield and I_a is the absorbed intensity in einsteins $\text{l}^{-1}\text{sec}^{-1}$. The expression is equivalent to that obtained for γ -irradiated systems and predicts that $\Phi(\text{acetaldehyde})$ should have no dependence on pH which agrees with experimental results.

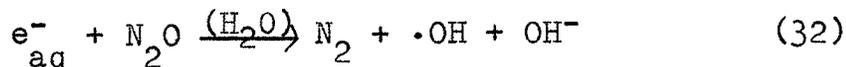
The observed values for $\Phi(\text{acetaldehyde})$ can be considered another manifestation of the dose rate effect already discussed in the previous section. The chain lengths are longer under photochemical initiation because the rate of initiation has been reduced. Experimentally the ratio $\Phi(\text{acetaldehyde})/G(\text{acetaldehyde})$ equals .61 at pH 6 and at glycol concentration 1.8 M. On the basis of equations (88a) and (97) one would expect the ratio to be equal to

$$\sqrt{\Phi_{\text{OH}}/I_a \cdot D/G_R} \text{ or } 0.54 \quad \Phi_{\text{OH}} = 1.0 \quad (19)$$

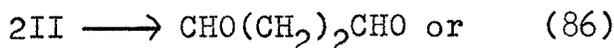
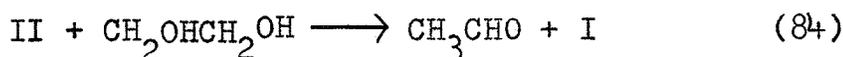
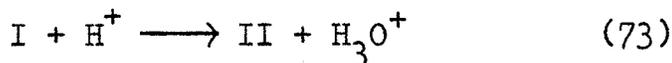
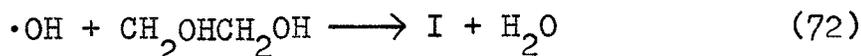
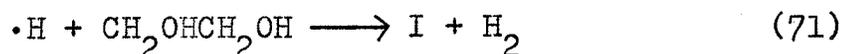
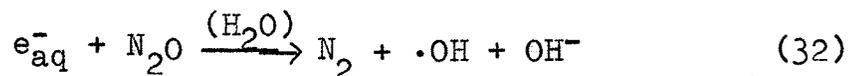
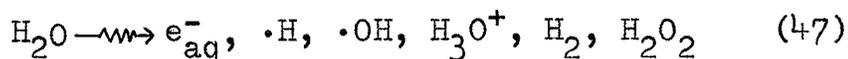
The experimental values of acetaldehyde yield are thus still larger than predicted from the proposed mechanism but at the lower dose rate used in this experiment the difference is approaching that permitted by experimental error.

B. Ethylene Glycol-N₂O in Deaerated Aqueous Solution

With nitrous oxide in the system in place of the hydrogen peroxide the hydrated electrons are believed to react as follows:



As before, the $\cdot\text{H}$ and $\cdot\text{OH}$ radicals formed from the interaction of the γ -rays with water and from reaction (32) react with ethylene glycol to produce radical I which can then rearrange. The radical conversion reaction (84) can take place but there should be no oxidative chain to compete with the rearrangement in neutral solution (39). The chain termination step probably consists of the reaction between two type II radicals. The proposed mechanism is summarized below.



acetaldehyde * acetic acid

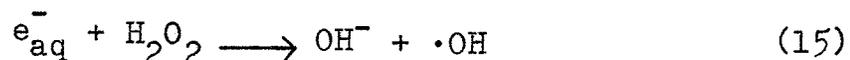
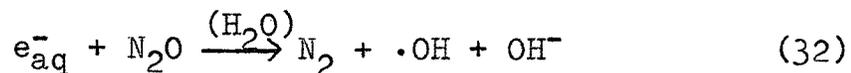
The expression for G(acetaldehyde) derived from this mechanism is identical to that obtained for the system containing hydrogen peroxide.

$$G(\text{acetaldehyde}) = k_{84} \sqrt{\frac{G_{e^-} + G_H + G_{OH}}{2k_{86}D}} [\text{glycol}] + \frac{G_{e^-} + G_H + G_{OH}}{2} \quad (88)$$

Equation (88) predicts a linear glycol dependence as observed experimentally. The fact that the slope obtained by plotting G(acetaldehyde) against glycol concentration was smaller for the N₂O system than that obtained for the H₂O₂ system, 5 vs. 7.6 respectively in the customary units, can only be attributed to experimental error. The large dose rate effects observed here cannot be explained at this time but they are probably due to the same causes as those observed in the peroxide system.

It should be emphasized that the mechanism proposed for the N₂O system is basically the same as that proposed for the H₂O₂ system. The fact that there is no reaction between radical I and N₂O is of little consequence because the oxidative chain was shown to occur independently of the chain pro-

ducing acetaldehyde. Reaction (32) is not essentially different from reaction (15) because in both processes hydrated electrons are scavenged and transformed into $\cdot\text{OH}$ radicals.

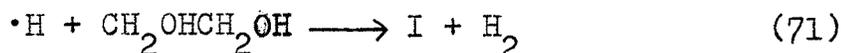
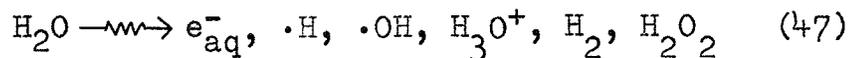


C. Ethylene Glycol- O_2 in Aqueous Solution

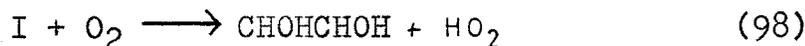
The results observed when systems containing oxygen were γ -irradiated can easily be explained on the basis of the proposed mechanism along with other known reactions of oxygen with organic and primary radicals. It was noticed that the concentration of the hydrogen peroxide produced reached a maximum and then fell off. Only after this maximum point was attained did acetaldehyde production proceed at a significant rate. In fact, after the hydrogen peroxide removal began the entire reaction seemed to proceed in an identical fashion to the deaerated system.

When the oxygen content was increased a larger dose was required to reach the maximum H_2O_2 concentration.

It is believed that reactions (47), (71), and (72) occur as expected.



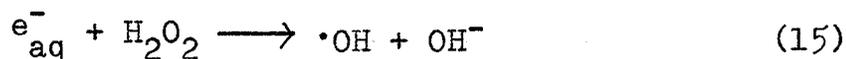
The oxygen will react with the hydrated electrons and radical I formed in reactions (71) and (72) and compete for $\cdot\text{H}$ atoms with reaction (71).



Thus the rearrangement is inhibited, oxygen is consumed and peroxide produced until

$$k_{15} [e_{\text{aq}}^-] [\text{H}_2\text{O}_2] > k_{54} [e_{\text{aq}}^-] [\text{O}_2]$$

when reaction (15) becomes dominant.



As the concentration of oxygen decreases further its reactions make an insignificant contribution to the overall mechanism and the system behaves in the same way as a deaerated one. Obviously a larger dose will be required to reach the peroxide maximum point when

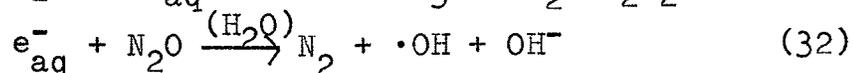
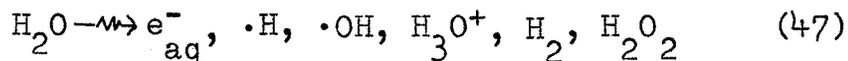
there is more oxygen to be consumed. The fact that the peroxide destruction is first order is probably fortuitous because at this low a concentration of peroxide the approximation used to derive equation (93) is probably invalid.

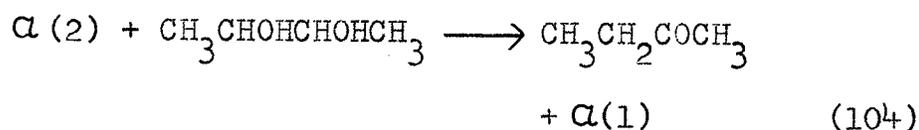
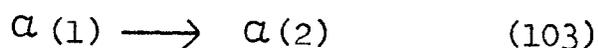
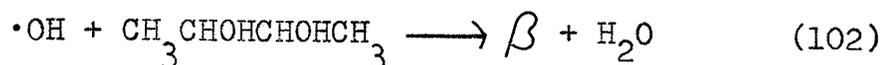
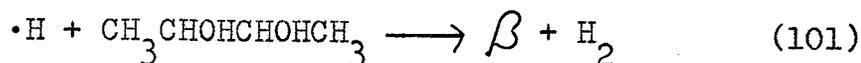
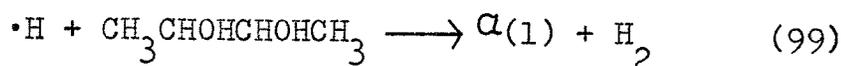
D. Other Glycols in Deaerated Aqueous Solution

4.8 Butane-2,3-diol

The fact that methyl ethyl ketone was produced from butane 2,3 diol indicates that the rearrangement is not limited solely to ethylene glycol but is possibly a general reaction for glycols. The N_2O system showed a glycol concentration dependence indicating that the mechanism involved bears certain features in common with the mechanism for ethylene glycol rearrangement. The non-linearity of this dependence, the additional gas chromatograph peaks, and the unresolved, almost random behavior of the peroxide system testify to the increased complexity of the system over that of ethylene glycol.

Some of the probable steps in the N_2O system are listed as follows:



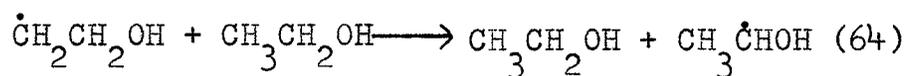
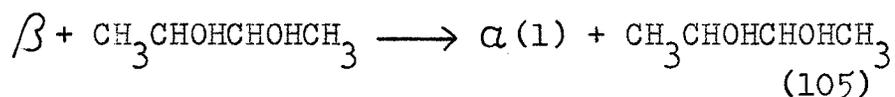


$\alpha(1)$ represents $\text{CH}_3\dot{\text{C}}\text{HOHCHOHCH}_3$, β represents $\dot{\text{C}}\text{H}_2\text{CHOHCHOHCH}_3$, and $\alpha(2)$ represents $\text{CH}_3\dot{\text{C}}\text{HCOCH}_3$.

The above reactions account for the rearranged product and for the dependence of G(methyl ethyl ketone) on butane-2,3-diol concentration. That these reactions do occur is supported by e.s.r. data. The β and $\alpha(2)$ radicals have been identified by Buley, Norman, and Pritchett (46) in a flow system 0.02 sec. after mixing butane-2,3-diol and a solution 0.02 M in titanous ion and 0.1 M in hydrogen peroxide. The experiment was performed at pH 0 where the rearrangement was undoubtedly so fast that the radical $\alpha(1)$ was too short-lived to be detected. The mechanism clearly contains all the features of that for ethylene glycol with the addition of the occurrence of

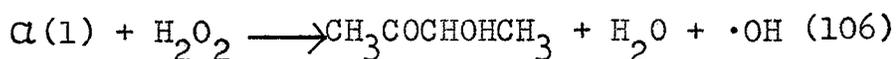
α and β -radicals.

One can only speculate on the fate of the β -radicals. They may undergo the radical conversion reaction (105) similar to the reaction described by Burchill and Ginns (27) for ethanol.



Such a reaction could account for the non-linear dependence of the reaction on glycol concentration if both reactions (104) and (105) must compete with terminating steps involving $\alpha(2)$ and β respectively.

The terminating step could also consist of two $\alpha(1)$ radicals and/or any combination of $\alpha(1)$ with $\alpha(2)$ and β . In addition, in a system containing peroxide reaction (106) probably occurs in competition with reaction (103).



The fact that the peroxide concentration in the stock solution decreased with time suggests that thermal oxidations also occur.

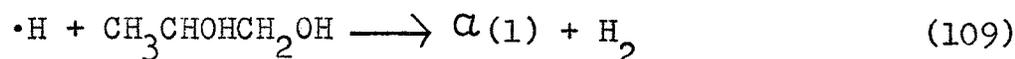
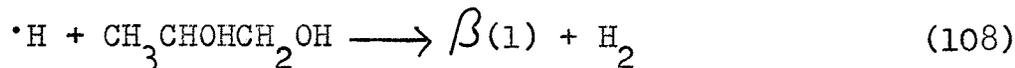
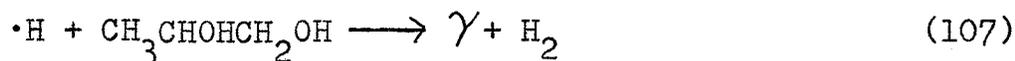
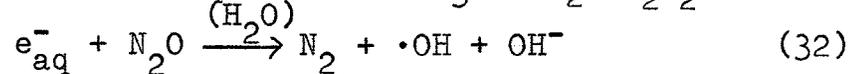
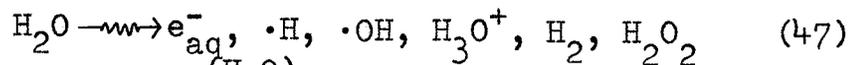
Some of the unidentified gas chromatograph peaks were very large and had short retention times.

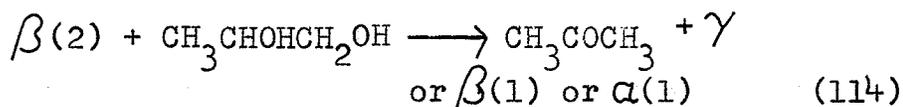
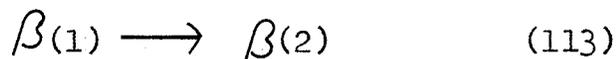
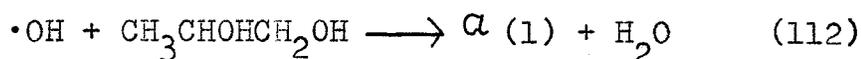
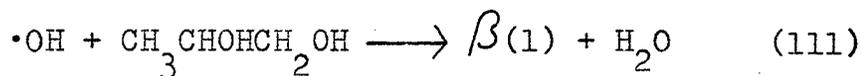
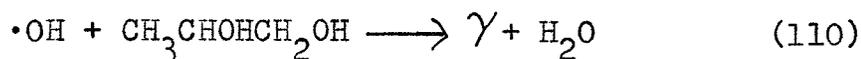
These peaks may be due to alkanes produced by reactions involving methyl radicals formed by direct interaction between butane-2,3-diol and the γ -radiation.

4.9 Propylene Glycol

The production of acetone in significant quantities by irradiating propylene glycol solutions is further evidence for the generality of the rearrangement. The situation here is still more complex than for butane-2,3-diol as more radical species are possible. However, there does not appear to be any thermal oxidations because the destruction of hydrogen peroxide was first order in peroxide.

A mechanism analogous to that proposed for the two glycols discussed previously can be used to explain the acetone production. The mechanism which indicates only some of the possible reactions demonstrates the cause of the complexity of this system.





γ represents $\dot{\text{C}}\text{H}_2\text{CHOHCH}_2\text{OH}$, $\beta(1)$ represents $\dot{\text{C}}\text{H}_3\text{CHOHCH}_2\text{OH}$, $\alpha(1)$ represents $\text{CH}_3\text{CHOH}\dot{\text{C}}\text{HOH}$, and $\beta(2)$ represents $\text{CH}_3\text{CO}\dot{\text{C}}\text{H}$.

Some evidence can be offered to support the above reactions. E.s.r. spectra taken in a manner similar to that used in examining the butane-2,3-diol system have shown the existence of the γ and $\beta(2)$ radicals. Buley, Norman, and Pritchett (46) studied the propylene glycol system at pH 0 where $\beta(1)$ would probably be too short-lived to be detected. These authors did not observe the $\alpha(1)$ radical nor did they observe the radical $\alpha(2)$, $\text{CH}_3\dot{\text{C}}\text{HCHO}$, which might be expected if $\alpha(1)$ rearranged.

In a hydrogen peroxide system either the $\beta(1)$ or $\alpha(1)$ -radicals could be oxidized to their corresponding hydroxy ketone or aldehyde. If both

the $\alpha(1)$ and $\alpha(2)$ radicals do exist then there are 15 combinations possible as termination steps. Obviously a great deal of work is required to unravel the entire mechanism, however, it may be maintained on the grounds of e.s.r. data, the experimentally observed formation of acetone and first order destruction of peroxide, and the known behavior of primary radicals with organic compounds that the mechanism involved here is similar to that proposed for the ethylene glycol system.

E. Summary

A free radical chain rearrangement has been observed in aqueous glycol solutions. This rearrangement can be initiated by the photolysis of hydrogen peroxide or by the radiolysis of water. A mechanism was proposed and has proven capable of explaining almost all the observations made on the ethylene glycol system. The mechanism was also able to explain several significant features of the butane-2,3-diol and the propylene glycol systems. However, due to the complexity of these systems much remains uncertain concerning them.

5. Suggestions For Further Work

It was noted in chapter 3 that the dose-yielded curves for acetaldehyde do not pass through the origin. This may be because $G(\text{acetaldehyde})$ is temperature dependent. As the solutions absorb γ -rays their temperatures increase and a steady-state is perhaps not attained until a dose of about $8.4 \times 10^{21} \text{ eV l}^{-1}$ has been absorbed then the yields vary linearly with dose. Seidler and v. Sonntag (38) noticed that $G(\text{acetaldehyde})$ increased from 1.3 at ambient temperature to over 6 at 100°C in the system they studied. More work should be done to determine if this is the cause of the non-linearity of the dose-yield curves at low dose.

The hydrogen peroxide destruction was not stoichiometrically equivalent to the glycolic acid production. Other oxidation products such as oxalic acid or carbon dioxide could possibly be formed. These products should be completely determined.

In the preceding chapter it was described how $G(\text{acetaldehyde})$ increased several times when the pH was increased to about 9.2 and how the e.s.r. spectrum of the radicals changed in this region (42). It appears that a somewhat different mechanism is in

operation above pH 9 and research should be done to determine the nature of this mechanism.

A great deal of work must be done to determine all the products obtained when propylene glycol and butane-2,3-diol are irradiated in aqueous solution containing H_2O_2 or N_2O . Once the products are identified progress may be made in determining all the steps in these potentially complex mechanisms.

One of the questions that was very briefly examined was whether the rearrangement would occur in the case of 1,3 diols. Nothing very concrete can be said on this question at this time. It was hoped that some light would be shed on the problem if the peroxide destruction was followed when aqueous 1,3 propane diol containing H_2O_2 was irradiated. If the rearrangement mechanism occurred then peroxide destruction would be first order in peroxide whereas if simple oxidation with no rearrangement occurred then a zero order destruction would take place as in the case of 2-propanol. The results proved to be ambiguous. When 1.3 M 1,3 propane diol was used the peroxide destruction was zero order but when the concentration was decreased to .55 M the destruction seemed to be first order. In any event, to completely

answer the original question as to whether the rearrangement occurs when the OH groups are separated by a carbon atom all the irradiation products must be identified.

Another interesting question that remains to be settled is whether the rearrangement will take place in cyclic glycols and if so will it be favored by the trans or cis arrangement. If only one of the isomers rearranges then one can obtain information about the conformational requirements of the rearrangement.

If a little speculation be allowed in conclusion then mention might be made of applying this type of reaction to a problem in radiobiology. It is known that a dose of about $3 \times 10^{19} \text{ eV l}^{-1}$ may be sufficient to kill a man (2) and yet the effect of such an amount of radiation on an ordinary chemical may be almost undetectable. It is known that living cells are comprised of 85% water and it is also known that D.N.A. molecules, ultimately responsible for enzyme manufacture, have deoxyribose as a major constituent. R.N.A. which is believed to actually assemble the enzymes contains ribose.

Adjacent OH groups are present in both ribose and deoxyribose. These latter may undergo some kind of rearrangement under irradiation so that when they are assembled into a D.N.A. or R.N.A. molecule the phosphate links or the purine and pyrimidine bases do not connect up properly or at all. Thus, at the very least, the length of the D.N.A. or R.N.A. molecule is changed and also the genetic code incorporated into each. The enzymes produced by these defective molecules should be quite different from the normal variety and would probably be incapable of performing their biochemical tasks. In this way a small amount of radiation affecting certain chemicals directly could cause large-scale effects indirectly.

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