THE UNIVERSITY OF MANITOBA

THE GAMMA-RADIATION INDUCED OXIDATION OF 1,4-DIOXANE, TETRAHYDROFURAN AND 1,3-DIOXOLANE BY HYDROGEN PEROXIDE IN NEUTRAL AQUEOUS SOLUTIONS

by

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ABSTRACT

The gamma-radiation induced oxidation of tetrahydrofuran, 1,4-dioxane and 1,3-dioxolane by H_2O_2 in neutral solutions has been investigated. Tetrahydrofuran and 1,4-dioxane are oxidized to 2-tetrahydrofuranol and 1,4-dioxan-2-ol and the H_2O_2 is reduced in stoichiometrically equivalent yields. For all three ethers, the yields are independent of the ether concentration, the H_2O_2 concentration and the dose rate. Substitution of 3,3,4,4-d_4-tetrahydrofuran for tetrahydrofuran results in increased yields, while substitution of 2,2,3,3,5,5,6,6-d_8-1,4-dioxane for 1,4-dioxane does not affect the yields.

The results for tetrahydrofuran are explained by a mechanism in which initiation occurs via H-atom abstraction from tetrahydrofuran to form either the 2-tetrahydrofuranyl radical or the 3-tetrahydrofuranyl radical. The reaction of the 2-tetrahydrofuranyl radical with H_2O_2 results in chain propagation while the 3-tetrahydrofuranyl radical participates only in termination.

A mechanism that would account for the experimental results for the oxidation of 1,4-dioxane could not be found.

A mechanism for the oxidation of 1,3-dioxolane could not be proposed because the products of the reaction were not identified.

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1. INTRODUCTION

1.1 Scope and Purpose of the Experiment

In recent years, a great deal of work has been done on the free radical induced oxidation of simple organic compounds. Metal ion-H_2O_2 couples, as well as thermal, photochemical and radiation chemical methods have been used to initiate free radicals. The list of organic compounds, whose oxidation by a variety of oxidizing reagents has been studied, is large indeed. In order to understand the mechanism of these free radical oxidations, the need to study a large number of substrates, by a variety of techniques, is paramount.

A major investigation of the gamma-radiation induced oxidation of methanol, ethanol and 2-propanol by H_2O_2 in aqueous solutions was performed in this laboratory by Ginns(1). It is desirable to see if the mechanism proposed for the oxidation of this alcohol series can be applied to other similar organic compounds. A related group of compounds are the ethers. No work on the gamma-radiation induced H_2O_2 oxidation of ethers in aqueous solutions has been previously reported.

The major difficulty in studying ethers in aqueous systems is that the acyclic forms are only slightly soluble in water. However, 1,4-dioxane, tetrahydrofuran and 1,3-dioxolane are very soluble in water. 1,4-Dioxane can yield only α-radicals analagous to those from methanol. An α-radical is a free radical with the unpaired electron associated with the carbon atom to which a functional group is bonded. Similar to 2-propanol, tetrahydrofuran can yield both an α-radical and a β-radical. A β-radical is a free radical with the unpaired electron associated with the carbon atom adjacent to the carbon atom to which a functional group is bonded. 1,3-Dioxolane, although it can form no β-radical, can form two different types of α-radicals. These cyclic ethers were chosen for the investigation.

Since the experiments entailed the gamma-irradiation of aqueous solutions, an explanation of some aspects of radiation chemistry is necessary to completely understand the interpretation of the results. A brief discussion of radiation chemistry is given in the following section.

1.2 Radiation Chemistry Background

A comprehensive discussion of radiation chemistry is not necessary because there are numerous published works dealing with the manifold facets of radiation chemistry (2-8).

When gamma-radiation passes through matter of low atomic weight, the energy is absorbed by the material predominately through a process called Compton Scattering. Compton Scattering is an elastic collision between the incident photon and an atomic electron resulting in the ejection of a fast electron and a deflected photon. This process is non-specific. The energy transferred to the medium from the ejected electron is responsible for the majority of radiation induced chemical reactions.

The prime absorber of energy in dilute aqueous systems is the bulk solvent. After absorption of the energy by water, a series of chemical reactions takes place such that, 10^{-9} s after the passage of the radiation, the following species are present: H, OH, e^-_{aq}, H_2O_2, H_2, H_3O^+. The radiation chemistry of water and aqueous solutions is explainable in terms of these species. Excellent reviews of the radiation chemistry of water and aqueous solutions have been done by Buxton (7) and Draganic and Draganic (8).

The absorbed dose of any ionizing radiation is the energy imparted to matter by ionizing particles per unit mass of irradiated matter at the place of interest (4). In this work the absorbed dose is expressed in units of electron-volts per liter (eV l^{-1}). The absorbed dose rate (D) is then the absorbed dose per unit time and has the units eV l^{-1} s^{-1}.

Yields in radiation chemistry, denoted by G values, are expressed in terms of the amount of energy absorbed. A

G value denotes the number of molecules changed for each 100 eV of energy absorbed. The symbol, G_x, refers to the primary radiation yield of x, while the symbol G(x) refers to the experimentally found yield of x after the chemical reaction is complete. The loss of material x that is destroyed on irradiation is symbolized G(-x).

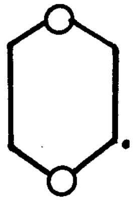
The product of a G value and a dose rate ($G_x D$ or G(x)D) is the concentration of x formed per unit time.

1.3 Related Studies

Although a similar system to the one studied has not been reported, some related studies have been done. Before the conclusion of this investigation, two closely related studies were reported by Walling, El-Taliawi and Johnson (9), and Gilbert, Norman and Sealy (11).

Walling, El-Taliawi and Johnson (9), using Fenton's reagent to generate radicals, studied the oxidation of 1,4-dioxane and THF by H_2O_2. The results were explained by mechanisms in which 1,4-dioxane yielded one radical species, easily oxidized by H_2O_2 and Fe^{3+}, while THF yielded two radical species only one of which was oxidized. For THF, the initial radical concentration ratio $[\alpha]/[\beta]$, was 6.2. These results confirmed those of Shono, Kuni and Oda (10). They found that the Fenton oxidation of 1,4-dioxane and THF yielded ∝ -hydroxy ethers and hydroxylated dimers as products.

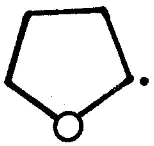
Gilbert, Norman and Sealy (11) used e.s.r. spectroscopy to investigate the reaction of the hydroxyl radical with ethers and alcohols, and the oxidation of the hydroxy- and alkoxy- conjugated radicals with hydrogen peroxide. The Ti(III)-H_2O_2 couple was used to generate radicals, and the rate constants of their reactions with hydrogen peroxide were estimated by the application of a competitive kinetic method. The reaction of the hydroxyl radical with 1,4-dioxane gave only the 1,4-dioxanyl radical, I, as previously reported (12-15), for which the rate constant for the oxidation of I by H_2O_2, $k_{(1)}$, was calculated to be $1.0 \times 10^5\ M^{-1} s^{-1}$.



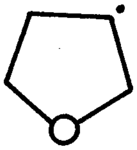
I

$$(1)\quad I + H_2O_2 \longrightarrow \text{molecular products} + OH$$

Oxidation of THF gave two radicals, previously identified as II and III (12, 16), in an initial radical concentration ratio, [II] / [III] of 6.0.



II



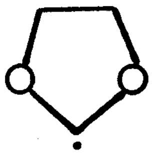
III

Increasing the Ti(III) concentration, at a constant H_2O_2 concentration, resulted in an increase in the radical concentration ratio, [II] / [III] .

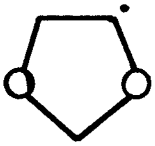
Assuming II is preferentially oxidized by H_2O_2, the rate constant, $k_{(2)}$, was calculated to be $4 \times 10^{4}\ M^{-1}\ s^{-1}$.

(2) $II + H_2O_2 \longrightarrow$ molecular products + OH

Two previously identified radicals, IV and V (16, 17), were observed for 1,3-dioxolane. The initial radical concentration ratio, [III] / [II] , was 1.18 at a H_2O_2 concentration of 3.5×10^{-3} M, and increased to 2.15 at a H_2O_2 concentration of 5×10^{-2} M.



IV



V

Assuming the preferential oxidation of IV at a very low H_2O_2 concentration, the rate constant for the reaction of IV with H_2O_2, $k_{(3)}$, was estimated to be 6 x 10^4 M^{-1} s^{-1}. This value should be regarded as a lower limit.

(3) $IV + H_2O_2 \longrightarrow$ molecular products + OH

The preferential oxidation of II by H_2O_2 had previously been used by Burchill and Jones (18) to explain their results. Photo-irradiation of an aqueous solution of acetone and THF gave an e.s.r. spectrum corresponding to two radicals identified as I and VI.

$$(CH_3)_2\dot{C}OH$$

VI

In the presence of H_2O_2, the spectrum of III was also present. At a low H_2O_2 concentration, the spectrum of VI disappeared while the concentration of II increased, and the spectrum of III appeared. As the H_2O_2 concentration was increased there was a gradual inversion of the concentration of II and III. They also reported that the gamma-irradiation of a deareated aqueous solution of THF and H_2O_2 gave a value of 29 for $G(-H_2O_2)$ suggesting the occurence of a chain reaction.

An investigation of the gamma-radiation induced oxidation of methanol, ethanol, and 2-propanol by H_2O_2 in aqueous solutions was reported by Burchill and Ginns (19, 20). The oxidation of methanol was explained by a simple mechanism.

$$(4)\quad H_2O \rightsquigarrow e^-_{aq},\ H,\ OH,\ H_3O^+,\ H_2O_2,\ H_2$$

$$(5)\quad e^-_{aq} + H_2O_2 \longrightarrow OH + OH^-$$

$$(6)\quad H + CH_3OH \longrightarrow H_2 + \underset{\text{VII}}{\cdot CH_2OH}$$

$$(7)\quad OH + CH_3OH \longrightarrow H_2O + \text{VII}$$

$$(8)\quad \text{VII} + H_2O_2 \longrightarrow HCHO + H_2O + OH$$

$$(9)\quad 2\ \text{VII} \longrightarrow \text{termination products}$$

Using the usual steady state assumption, the equation for H_2O_2 removal is:

$$(10)\quad \frac{-d\left[H_2O_2\right]}{dt} = \left(G_{e^-_{aq}} - G_{H_2O_2}\right) D + k_8 \frac{\left[\left(G_{e^-_{aq}} + G_H + G_{OH}\right) D\right]^{\frac{1}{2}}}{2k_9} \left[H_2O_2\right]$$

This equation predicts the rate of H_2O_2 removal to be independent of the alcohol concentration, dependent on the square root of the dose rate and first order in H_2O_2 concentration. This was in good agreement with the experimental results.

Ethanol and 2-propanol can yield two different types of radicals. Therefore, a more complex mechanism was needed to explain their oxidation.

(4) $$H_2O \rightsquigarrow e^-_{aq}, H, OH, H_3O^+, H_2O_2, H_2$$

(5) $$e^-_{aq} + H_2O_2 \longrightarrow OH + OH^-$$

(11) $$H + (CH_3)_2CHOH \longrightarrow H_2 + (CH_3)_2\dot{C}OH$$

VI

(12) $$OH + (CH_3)_2CHOH \longrightarrow H_2O + VI$$

(13) $$VI + H_2O_2 \longrightarrow (CH_3)_2CO + OH + H_2O$$

(14) $$H + (CH_3)_2CHOH \longrightarrow H_2 + \cdot CH_2CH_3CHOH$$

VIII

(15) $$OH + (CH_3)_2CHOH \longrightarrow H_2O + VIII$$

(16) $$VIII + (CH_3)_2CHOH \longrightarrow VI + (CH_3)_2CHOH$$

(17) 2 VIII $\longrightarrow$ termination products

Using steady state assumptions, an expression for the radiation chemical yield can be derived.

(18) $$G(-H_2O_2) = G_{e^-_{aq}} - G_{H_2O_2} + G_H\left\{\frac{k_{11}(k_{12} + k_{15})}{k_{15}(k_{11} + k_{14})}\right\} + \frac{k_{12}}{k_{13}}(G_{e^-_{aq}} + G_{OH}) + \left\{1 + \frac{k_{12}}{k_{13}}\right\}k_{16}\left(\frac{G_{e^-_{aq}} + G_H + G_{OH}}{2k_{17}D}\right)^{\frac{1}{2}}\left[\text{2-propanol}\right]$$

The equation predicts a first order dependence on 2-propanol or ethanol concentration, a square root dependence on dose rate, and no dependence on H_2O_2 concentration.

1.4 Summary

On the basis of Ginns' work (1, 19, 20) with primary and secondary alcohols and the related studies on cyclic ethers, the expectations for the mechanism of gamma-radiation induced H_2O_2 oxidation of cyclic ethers is summarized below.

Gamma-irradiation of 1,4-dioxane, in the presence of H_2O_2, should give rise to only one radical species, an

α-radical, which is oxidizable by H_2O_2 to 1,4-dioxan-2-ol. The kinetics of the reactions should be characterized by:

a) no dependence on ether concentration.

b) first order in peroxide concentration.

c) a square root dependence on dose rate.

d) no effect by deuterium substitution on 1,4-dioxane.

In contrast, THF, irradiated in the presence of H_2O_2, should yield two radicals; an α-radical that can be oxidized by H_2O_2 to 2-tetrahydrofuranol and a β-radical that can take part only in termination. The dependence on ether concentration as found for ethanol and 2-propanol is unlikely because a reaction such as (19)

(19) $\text{III} + \text{THF} \longrightarrow \text{II} + \text{THF}$

would not be as probable as one like (16). In reaction (19), the abstraction of a H-atom from the methylene group in the α-position by the β-radical results in the formation of a methylene group in the β-position; while, in reaction (16) the abstraction of the single H-atom in the α-position by the β-radical yields a terminal methyl group. There should be no effect of H_2O_2 concentration. However, deuterium substitution at the β-positions should result in an increased rate of reaction while deuterium substitution at the α-positions should retard the reaction rate.

1,3-Dioxolane with two radicals of the α-type possible, both oxidizable by H_2O_2, should follow a kinetic scheme too complex for the scope of this investigation.

The results of the experiments did not conform to all these expectations.

2. EXPERIMENTAL

2.1 Radiolysis Experiments

2.1.1 Materials

Triply distilled water was produced by distilling laboratory distilled water from a potassium permanganate solution and then redistilling the distillate from a potassium dichromate solution.

Hydrogen Peroxide (Fisher Certified 30%) was used as received.

1,4-Dioxane (Fisher Certified) was used as received except when peroxides were present. The peroxides were removed by passing the ether through a column of activated alumina. Peroxides were detected and their removal was monitored by the triiodide method (28).

1,3-Dioxolane (Eastman Chemicals) was used as received.

Tetrahydrofuran (Baker Analysed) was used as received.

Tetrahydrofuran (Fisher Histological) was purified by refluxing with, then distilling from lithium aluminum hydride.

3,3, 4,4-d_4-Tetrahydrofuran (Merck, Sharpe and

Dohme) was used as received.

2,2, 3,3, 5,5, 6,6-d_8-1,4-Dioxane (Merck, Sharpe and Dohme) was used as received.

Reagent grade chemicals were used for dosimetry without further purification.

2.1.2 Irradiation Facilities

A ^{60}Co Gammacell 220 was used for all the radiolysis experiments. The Gammacell, cell holder and method of attenuation were described by Hickling (21).

The dose rates for January 1974 are shown in Table 2.1.

TABLE 2.1

Dose Rates for Gammacell 220

Attenuation, %	Dose Rate, eV l^{-1} s^{-1}
100	8.50×10^{18}
30	2.33×10^{18}
10	7.21×10^{17}

2.1.3 Dosimetry

The dose rate was measured with the Fricke dosimeter, an air saturated solution of 10^{-3} M $FeSO_4(NH_4)_2SO_4 \cdot 6H_2O$ in 0.4M H_2SO_4. Five ml of the solution was passed into each sample bulb, then each bulb was irradiated for a different length of time. Under irradiation the ferrous ion is oxidized to ferric ion. The concentration of Fe^{3+} was measured spectrophotometrically at 305 nm using a Carl Zeiss PMQ II spectrophotometer. The molar extinction coefficient was assumed to be $2.2 \times 10^3\ M^{-1}\ cm^{-1}$ and $G(Fe^{3+})$ was taken as 15.6 ions/100 eV. The dose rates were measured at the beginning and at the end of this research. Once the dose rate was established, the value for a particular experiment was determined from a chart that tabulated the decay of ^{60}Co. The chart was provided by A.E.C.L. with the Gammacell 220.

2.1.4 Sample Preparation

All glassware was cleaned by rinsing with chemicals in the following sequence: water, permanganic acid, nitric acid containing a few drops of H_2O_2, distilled water (seven times), triply distilled water (three times). The clean irradiation bulbs were allowed to drip dry overnight.

The stock solution was prepared by adding the appropriate volume of ether to a 100 ml volumetric flask, half-filling the flask with triply distilled water, then adding the H_2O_2 and bringing the solution up to volume with triply distilled water. To prepare irradiation samples, 5 ml aliquots of the stock solution were transferred to clean dry 25 ml pyrex bulbs. The sample bulbs were attached with tap assemblies to a vacuum line for degassing. The procedure has been previously outlined (21). The samples were degassed by three freeze-pump thaw cycles, irradiated, then immediately analysed for H_2O_2.

2.2 Analysis Techniques

2.2.1 Materials

Methanol (Fisher Certified) was purified by refluxing with 2,2-dinitrophenylhydrazine in an acidic medium followed by distillation through a "Vigreaux" column. The carbonyl-free methanol remained good for one to two months.

2,4-Dinitrophenylhydrazine (BDH Chemicals) was twice recrystallized from the pure methanol. It was recrystallized as needed.

Potassium hydroxide solution was prepared by dissolving 10 g KOH (Fisher Certified) in 20 ml triply distilled water, then bringing the volume up to 100 ml with pure methanol.

2,4-Dinitrophenylhydrazine (2,4-DNPH) solution was prepared by suspending 2 g of 2,4-DNPH in 100 ml pure methanol, then adding with stirring 4 ml concentrated H_2SO_4. The solution was filtered before use. The solution was prepared as needed.

1,4-Dioxene (Aldrich Chemicals) was used as received.

Reagent grade chemicals were used as received for the analysis of hydrogen peroxide.

2.2.2 Preparation of 1,4-Dioxan-2-ol, 2-Tetrahydrofuranol and their 2,4-Dinitrophenylhydrazones

1,4-Dioxan-2-ol and 2-tetrahydrofuranol were both synthesised by two methods.

1,4-Dioxan-2-ol Method I:

Acid hydration of 1,4-dioxene yields 1,4-dioxan-2-ol (22). A solution of 10 ml of 1,4-dioxene and 25 ml 0.2N HCl was refluxed with constant stirring until the solution became homogeneous (approximately one hour).

The solution was cooled, neutralized with 10% KOH, and reduced in volume until the salt began to precipitate. After extraction with chloroform, drying over magnesium sulfate, and evaporation of the solvent, the residue was distilled under 12 mm pressure.

The product, in 60% yield, was collected at 90-91° C (Lit. 90-90.5° C/11 mm (10), 91-92° C/12 mm (22), 99° C/11 mm (25)). The distillate was clear and when cooled formed needle-like crystals, m.p. 30-31° C (Lit. 30° C (10), 35-36° C (22), 39° C (25)).

The nmr spectrum of the product with undeuterated chloroform as the solvent, was in good agreement with one reported by Gierer and Petersson (23).

1,4-Dioxan-2-ol Method II:

50 ml of 1,4-dioxane were put into a 1000 ml graduated erlennmeyer flask. The flask was then half-filled with triply distilled water and 2 ml of 30% H_2O_2 was added before the solution was brought up to volume with water.

A two-holed rubber stopper, which had a piece of glass tubing in one hole and a sintered glass gas outlet connected to an argon cylinder in the other hole, was put into place in the flask. The solution was degassed by bubbling argon through it for thirty minutes. The two pieces of glass tubing were then sealed and the solution was irradiated for seventy-five minutes.

After irradiation, the excess water was distilled off under reduced pressure until approximately 50 ml of solution were left in the flask. After extraction with chloroform, drying over magnesium sulfate and evaporation of the solvent, the residue was distilled under 12 mm pressure.

The clear distillate, in 33% yield, on the basis of H_2O_2 added, was collected at 94-95°C. An nmr spectrum, Fig. 2.1, of the product in undeuterated chloroform was identical to the one obtained for the compound prepared by Method I.

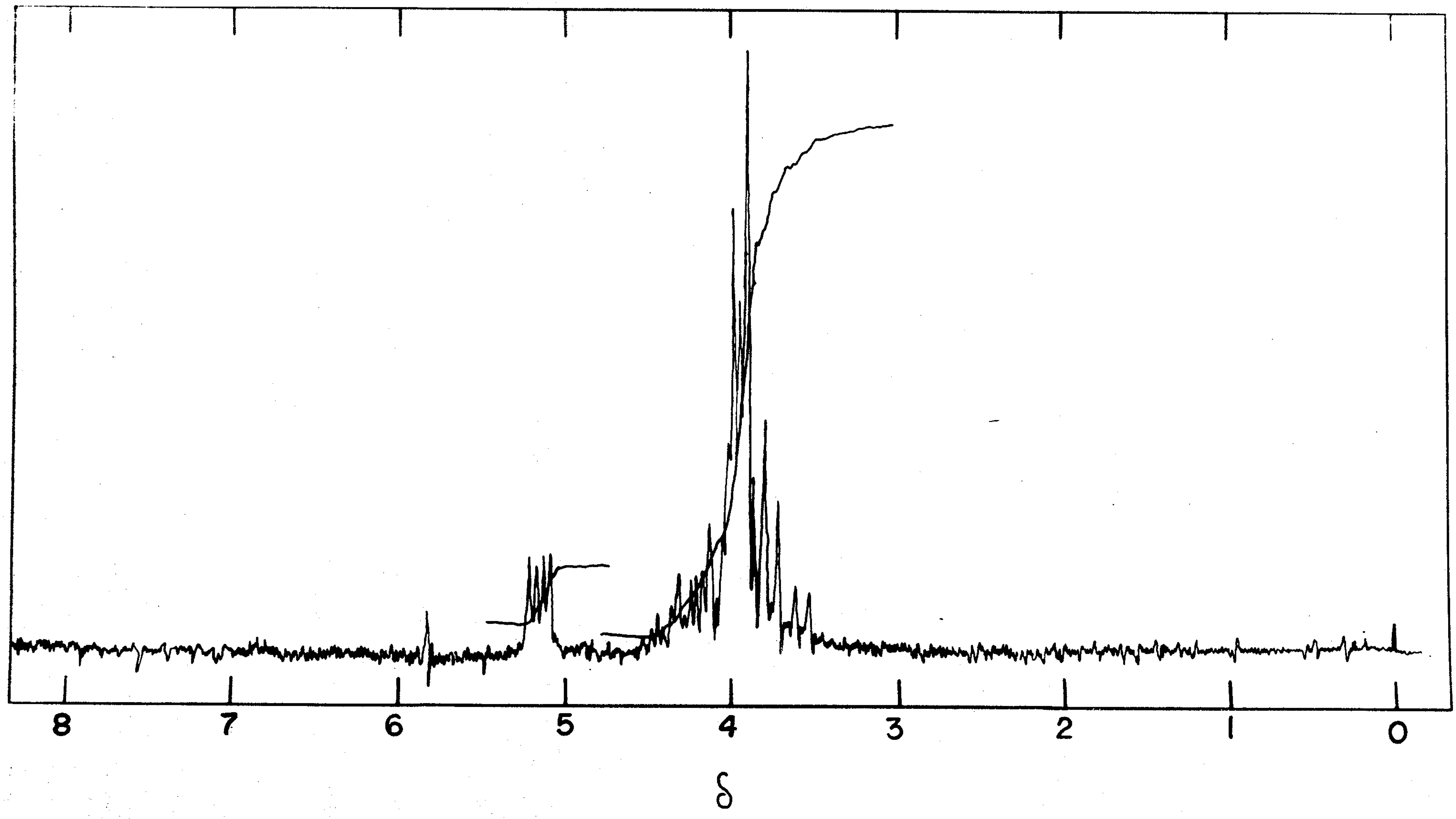
2,4-Dinitrophenylhydrazone of 1,4-Dioxan-2-ol

1,4-Dioxan-2-ol is a cyclic hemi-acetal that exists when in solution in equilibrium with the open chain hydroxy aldehyde form. In an acidic medium 2,4-dinitrophenylhydrazine reacts with the aldehyde group to form a hydrazone. This shifts the equilibrium in favor of the hydroxy aldehyde form resulting in the conversion of all the hemi-acetal to a 2,4-dinitrophenylhydrazone.

Enough 2,4-DNPH solution was added to the 1,4-dioxan-2-ol to have both the reactants present in equal molar quantities. The mixture was refluxed for thirty minutes. Upon cooling, the precipitate formed was filtered off and the filtrate diluted with water. The first precipitate did not melt up to 200°C. The second precipitate melted at 120-128°C. After successive filtrations, a precipitate that

Figure 2.1

The n.m.r. spectrum recorded for 1,4-dioxan-2-ol prepared by radiolysis of aqueous 0.6 M 1,4-dioxane containing 0.02 M H_2O_2. Undeuterated chloroform is the solvent.


8
7
6
5
4
3
2
1
0
δ

melted at 130-133°C was obtained. The orange-yellow crystals were purified by three recrystallizations, which did not change the melting point.

Thin-layer chromatography of the recrystallized product showed three spots. The final purified 2,4-dinitrophenylhydrazone of 1,4-dioxan-2-ol was obtained by thick layer chromatography. An acetone solution of the crystals was spotted on a plate of silica gel and developed with a 85% benzene-15% ether (V/V) solvent mixture. The large band nearest the origin was eluted with THF. The yellow crystals had a melting point of 133-135°C (Lit. 136-137°C (22, 24, 25)).

<u>2-Tetrahydrofuranol</u> <u>Method I</u>:

Fenton oxidation of THF was used to prepare 2-tetrahydrofuranol (10). A mole of THF was placed in a three-necked flask. Two cylinders, one containing 0.4M $FeSO_4$ solution, the other containing 0.4M H_2O_2, were placed in the two appropriate necks and a thermometer was placed in the third neck. The reaction flask was then placed in an ice bath sitting on a magnetic stirrer. The $FeSO_4$ and H_2O_2 were added at equal rates with constant stirring, while the temperature of the solution was maintained between 20-30°C. When the addition was complete, the solution was stirred for an additional fifteen minutes.

The solution was then filtered to remove the brown residue and the filtrate extracted with ether. After drying the extract over $MgSO_4$ and evaporating off the solvent, the remaining liquid was distilled over a "Vigreaux" column under 12 mm pressure. The liquid distilled off over a range of temperature. The fraction collected between 60-75 °C was analysed by nmr spectroscopy. The nmr spectrum, Fig. 2.2, was consistent with the structure of 2-tetrahydrofuranol.

The temperature range was the same as that found by Paul and Tchelitcheff (26) and Paul, Fluchaire and Collardeau(27), however, Shono, Kuni and Oda (10) determined the boiling point to be 70-70.5 °C/11 mm and Meerwin et al (25) found it to be 69-70 °C/14 mm. The yield was 1%.

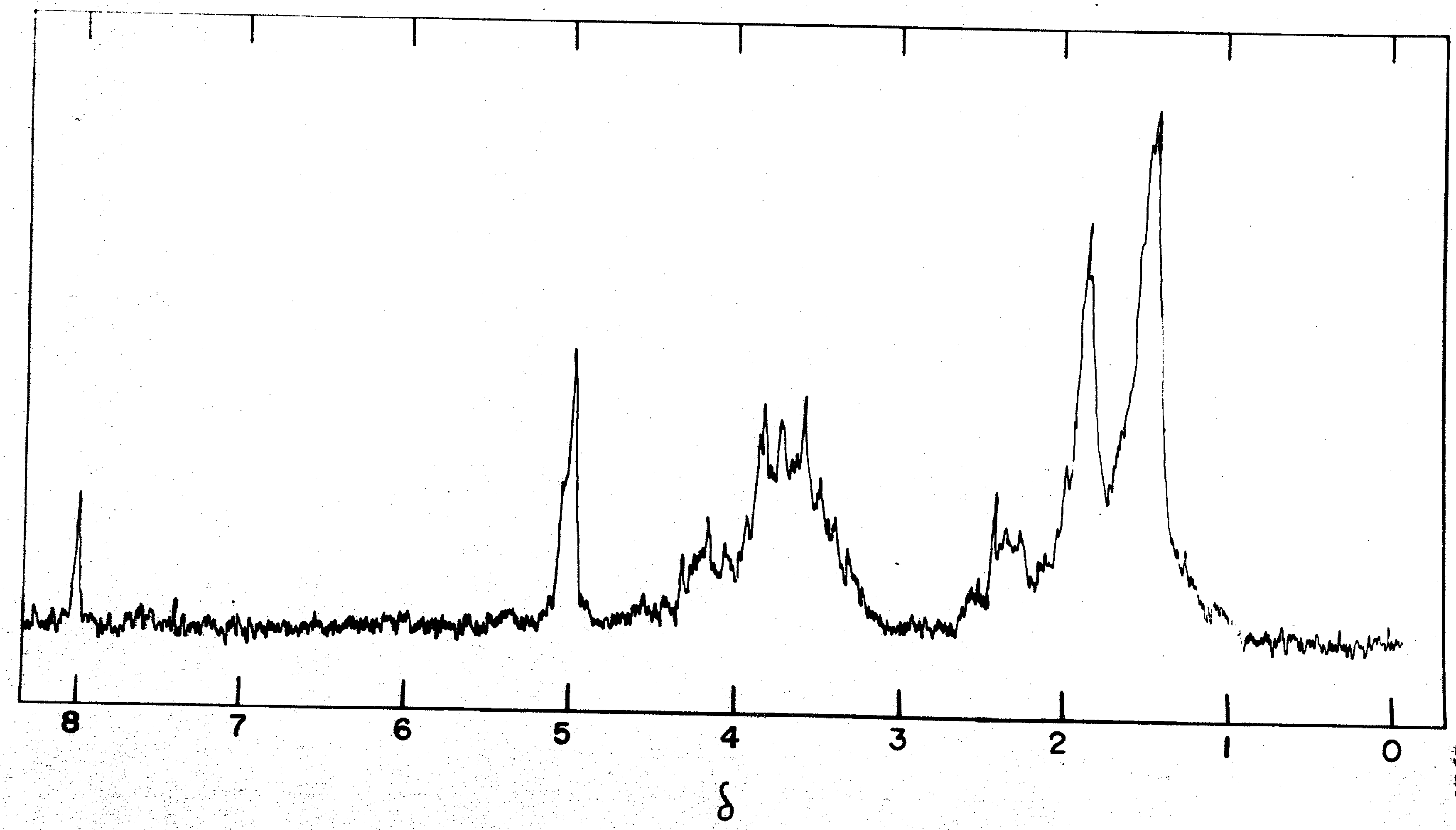
2-Tetrahydrofuranol Method II:

The same procedure was used as in Method II above for 1,4-dioxan-2-ol.

Again, the boiling point was variable, with the fraction between 60-75 °C collected at 12 mm pressure. The nmr spectrum, Fig. 2.3, agreed with the spectrum obtained for the product from Method I, Fig. 2.2.

Figure 2.2

The n.m.r. spectrum recorded for 2-tetrahydrofuranol prepared by Fenton oxidation of tetrahydrofuran. Undeuterated chloroform is the solvent.


8
7
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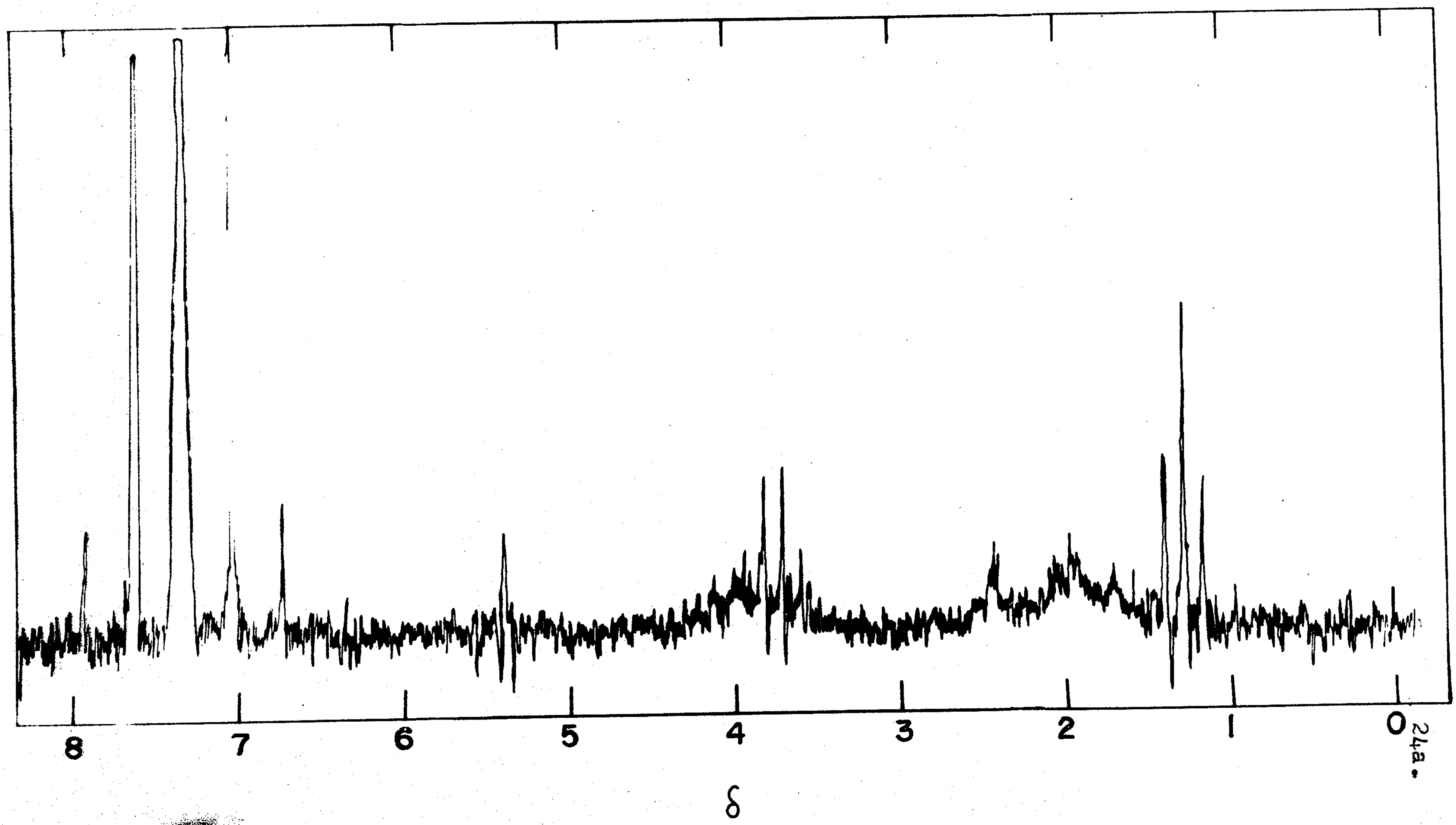
3
2
1
0
δ

Figure 2.3

The n.m.r. spectrum recorded for 2-tetrahydrofuranol prepared by radiolysis of aqueous 0.6 M tetrahydrofuran containing 0.02 M H_2O_2. Undeuterated chloroform is the solvent.


8
7
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5
4
3
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δ

2,4-Dinitrophenylhydrazone of 2-Tetrahydrofuranol

In an acidic solution, the reaction of 2-tetrahydrofuranol with 2,4-dinitrophenylhydrazone is analagous to the reaction of 1,4-dioxan-2-ol with 2,4-dinitrophenylhydrazone.

The 2,4-DNPH of 2-tetrahydrofuranol from Method I was prepared as described for 1,4-dioxan-2-ol. Only enough product could be isolated to characterize the compound by m.p., which was 111-115°C (Lit. 110-113°C (10), 118°C (26), 120°C (27)). The melting point of the 2,4-DNPH of 2-tetrahydrofuranol, from Method II, was 117-119°C.

2.2.3 Determination of the Molar Extinction Coefficient for the 2,4-Dinitrophenylhydrazones of 1,4-Dioxan-2-ol and 2-Tetrahydrofuranol

The molar extinction coefficient for the 2,4-dinitrophenylhydrazone of 1,4-dioxan-2-ol was determined by two methods but only one method was used for the 2,4-dinitrophenylhydrazone of 2-tetrahydrofuranol.

2,4-DNPH of 1,4-Dioxan-2-ol Method I:

The pure 2,4-DNPH of 1,4-dioxan-2-ol was dissolved in an appropriate volume of pure methanol. An aliquot of this solution was placed in a volumetric flask and diluted to volume with 10% KOH solution (29). The solution turned black. After allowing it to clear, the absorption spectrum was recorded on a Pye Unicam Sp 800 spectrophotometer, Fig. 2.4. The wavelength chosen for analysis was 530 nm and the absorbance was determined on a Carl Zeiss PMQ II spectrophotometer. The molar extinction coefficient was found to be $1.1 \times 10^4 M^{-1} cm^{-1}$.

2,4-DNPH of 1,4-Dioxan-2-ol Method II:

The 1,4-dioxan-2-ol was diluted to volume in pure methanol. An aliquot of this solution was refluxed with an appropriate volume of 2,4-DNPH and a few drops of HCl for thirty minutes. The solution was allowed to cool and an aliquot was diluted to volume with 10% KOH solution. The absorption spectrum was recorded on a Cary 14 spectrophotometer, Fig. 2.5. After allowing the solution to clear, the absorbance was read at 530 nm on a Carl Zeiss PMQ II spectrophotometer. The molar extinction coefficient was measured to be $1.0 \times 10^4 M^{-1} cm^{-1}$.

2,4-DNPH of 2-Tetrahydrofuranol

The molar extinction coefficient for the 2,4-DNPH of 2-tetrahydrofuranol was determined as in Method II above and found to be $4.0 \times 10^3 M^{-1} cm^{-1}$.

Figure 2.4

The absorption spectrum recorded for the 2,4-dinitrophenylhydrazone of 1,4-dioxan-2-ol in an alkaline methanol solution.

Molar Extinction Coefficient = $1.1 \times 10^{4}\ M^{-1}\ cm^{-1}$ at 530 nm

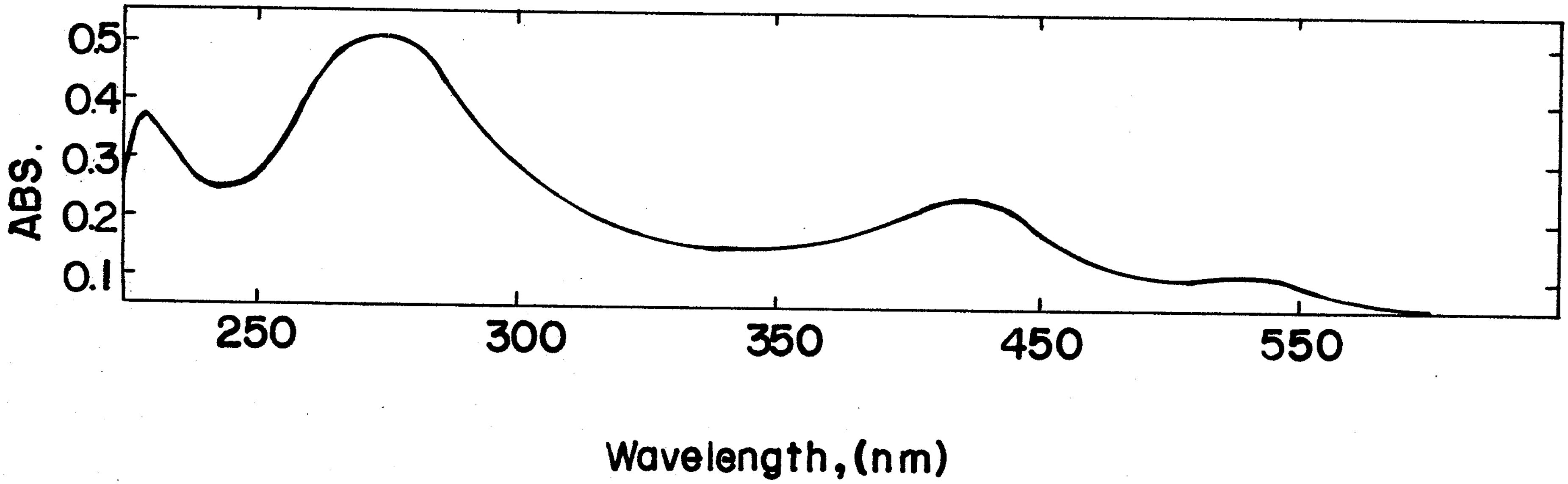
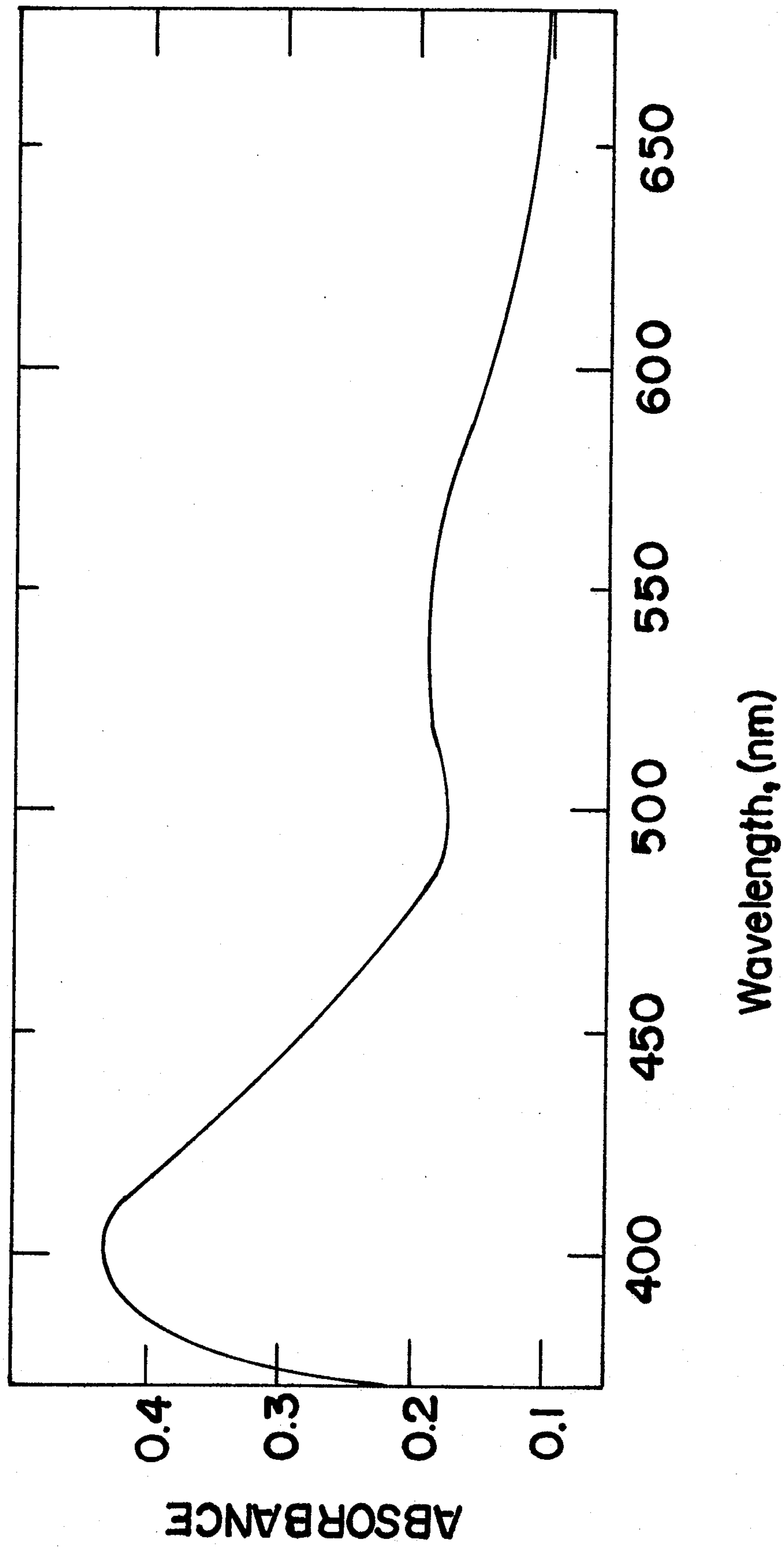

ABS.
0.5
0.4
0.3
0.2
0.1
250
300
350
450
550
Wavelength, (nm)

Figure 2.5

The absorption spectrum recorded for the 2,4-dinitrophenylhydrazone of 1,4-dioxan-2-ol as prepared by Method II.

Molar Extinction Coefficient = $1.0 \times 10^{4}\ M^{-1}\ cm^{-1}$


ABSORBANCE
0.4
0.3
0.2
0.1
400
450
500
550
600
650
Wavelength, (nm)

During the spectrophotometric determination of the 2,4-dinitrophenylhydrazones of both 1,4-dioxan-2-ol and 2-tetrahydrofuranol, the color of the solutions faded over a period of time; moreover, if the absorbance is read before the solution has completely cleared large changes in the absorbance occur rapidly. An example of the absorbance loss with respect to time for the 2,4-DNPH of 2-tetrahydrofuranol is shown in Table 2.2.

TABLE 2.2

Absorbance Loss with Time for the 2,4-DNPH of 2-Tetrahydrofuranol

Time(min)	Absorbance	% Loss
0	0.288	
5	0.268	6.9
10	0.253	12.2
18	0.234	18.7
27	0.215	25.3

The time interval between the addition of the KOH solution and the determination of the absorbance would have to be identical for each determination in order to achieve the optimum analytical accuracy. Although this was not done, reproducible results were obtained by placing the solution in the spectrophotometer as soon as it had cleared and then taking the first reading that only changed by 0.004 absorbance units in one minute as the absorbance of the solution.

2.2.4 Analytical Techniques

Hydrogen peroxide was measured by the triiodide method (28). An aliquot of the irradiated sample was added to 5 ml of potassium hydrogen phthalate buffer (12.5 g/500 ml H_2O). Then, 5 ml of iodide reagent (1.25 g NaOH; 41.5 g KI; 0.125 g $(NH_4)_6Mo_7O_{24}.4H_2O$/500 ml) was added and the solution was made up to volume with triply distilled water. The species formed, I_3^-, can be measured spectrophotometrically at 350 nm. The molar absorption coefficient was reported to be 2.5×10^4 M^{-1} cm^{-1} (28).

1,4-Dioxan-2-ol and 2-tetrahydrofuranol were both measured spectrophotometrically as their 2,4-dinitrophenylhydrazones (29). An aliquot of the irradiated sample was refluxed with 2,4-DNPH solution and a few drops of acid for thirty minutes. After cooling, an aliquot of the refluxed solution was placed in a 25 ml volumetric flask and made up to volume with KOH solution. The solution became very dark, but cleared quickly to a red color. The anion of the 2,4-DNPH was the species measured spectrophotometrically at 530 nm on a Carl Zeiss PMQ II spectrophotometer,(29).

3. RESULTS AND DISCUSSION - TETRAHYDROFURAN

3.1 Results

The gamma-radiation induced oxidation of tetrahydrofuran in deaerated aqueous solutions by hydrogen peroxide was investigated over a range of H_2O_2 and THF concentrations. The effects of dose rate and deuterium substitution on the reaction were also studied.

The samples were degassed to prevent inhibition of the chain reaction by the presence of oxygen.

THF/H_2O_2

The H_2O_2 removal yields at a constant THF concentration, 0.620M, are illustrated in a dose-yield plot, Fig. 3.1. The figure is a composite graph made up of results from runs with three different starting concentrations of H_2O_2. The removal yields are independent of the H_2O_2 concentration over the range 1.17×10^{-2} M to 3.56×10^{-2} M.

The THF used to obtain the above results was found to be contaminated with peroxide so the experiments were repeated for the initial concentrations of 1.86 and 3.56×10^{-2} M H_2O_2. The results are shown in Fig. 3.2. The H_2O_2 removal yields remain independent of the H_2O_2 concentration, but, the plot begins to curve at 1.00×10^{-2} M H_2O_2.

Figure 3.1

Gamma-radiation induced reduction of H_2O_2 in deaerated aqueous 0.620 M tetrahydrofuran.

Dose Rate = 10.24×10^{18} eV l^{-1} s^{-1}

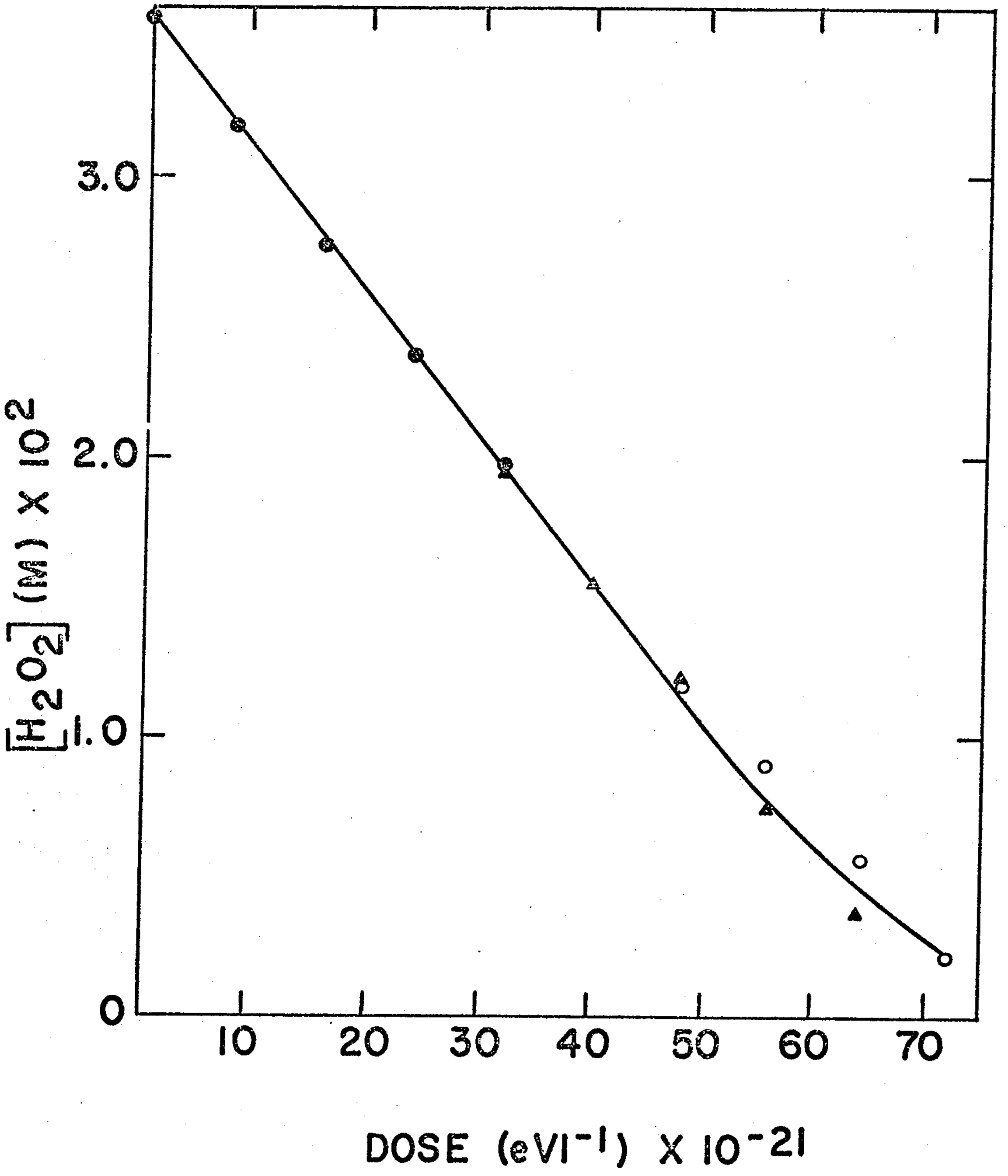
Initial H_2O_2 Concentration =

● ,0.036 M

▲ ,0.020 M

○ ,0.012 M

For each symbol, the initial point on the graph represents zero dose.



$[H_2O_2]$ (M) X 10^2
3.0
2.0
1.0
0
10
20
30
40
50
60
70
DOSE (eVl^{-1}) X 10^{-21}

Figure 3.2

Gamma-radiation induced reduction of H_2O_2 in deaerated aqueous 0.620 M tetrahydrofuran solution prepared with purified tetrahydrofuran.

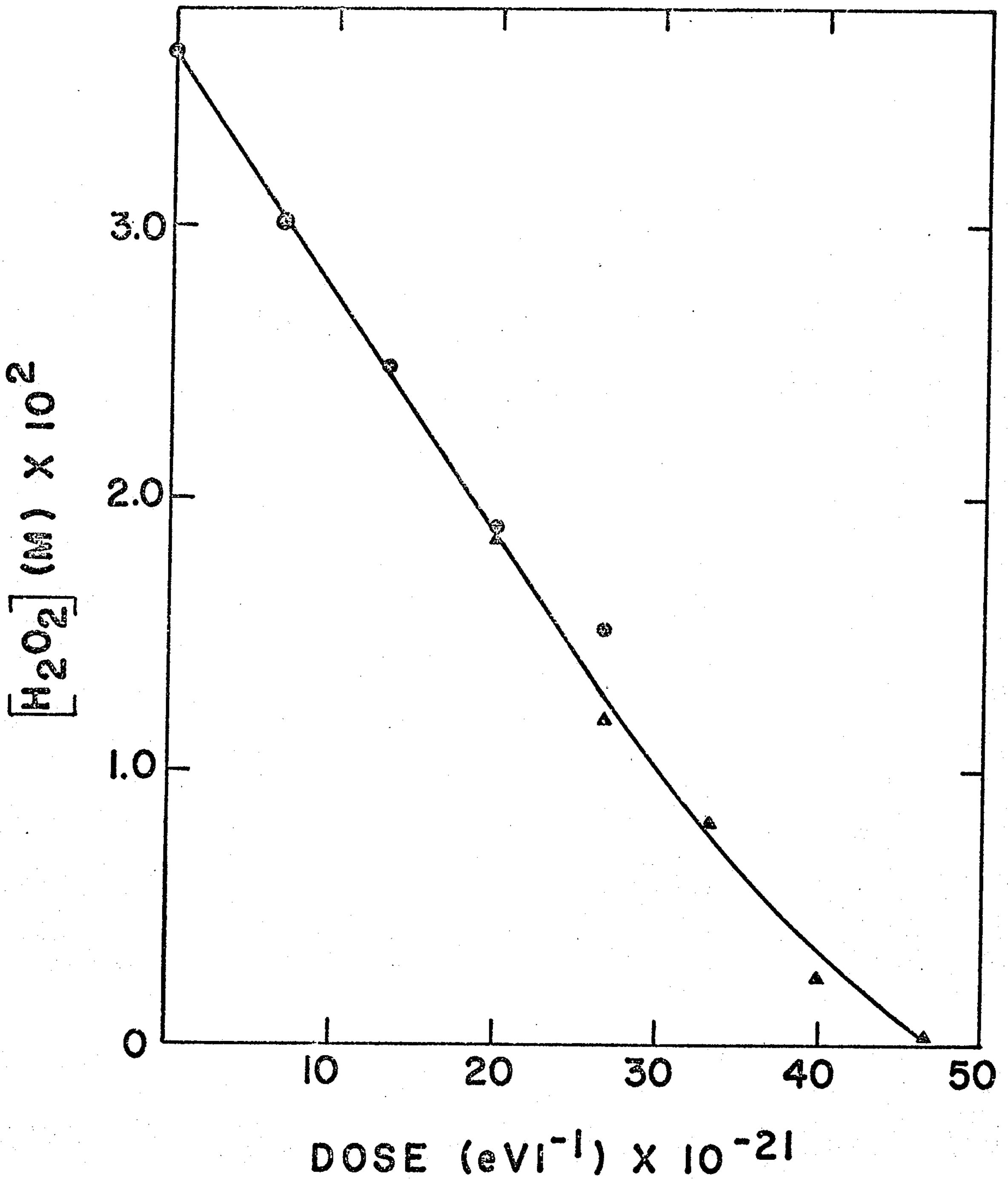
Dose Rate = 9.28×10^{18} eV l^{-1} s^{-1}

Initial H_2O_2 Concentration =

● ,0.036 M

▲ ,0.019 M

For each symbol, the initial point on the graph represents zero dose.


3.0
2.0
1.0
0
10
20
30
40
50
$[H_2O_2]$ (M) X 10^2
DOSE (eVl^{-1}) X 10^{-21}

A typical dose-yield plot is shown in Fig. 3.3. The initial linearity of the curve allows the accurate calculation of G-values, in this case, $G(-H_2O_2) = 29.9$. The stoichiometric equivalence between the H_2O_2 removal yield and the product formation yield was determined only at one value of dose because of the tediousness of the analytical procedure. At 18.5×10^{21} eV l^{-1}, $G(-H_2O_2) = 32.6 \pm 0.1$ and G(2-tetrahydrofuranol) = 34.5 ± 0.6. No attempt was made to identify the termination products.

Over the concentration range 0.124 M to 0.868 M THF, the H_2O_2 removal yields are independent of the THF concentration. This is illustrated in Table 3.1. The initial H_2O_2 concentration is 0.016 M and the dose rate is 9.18×10^{18} eV l^{-1} s^{-1}.

TABLE 3.1

Variation of H_2O_2 Removal Yields with THF Concentrations

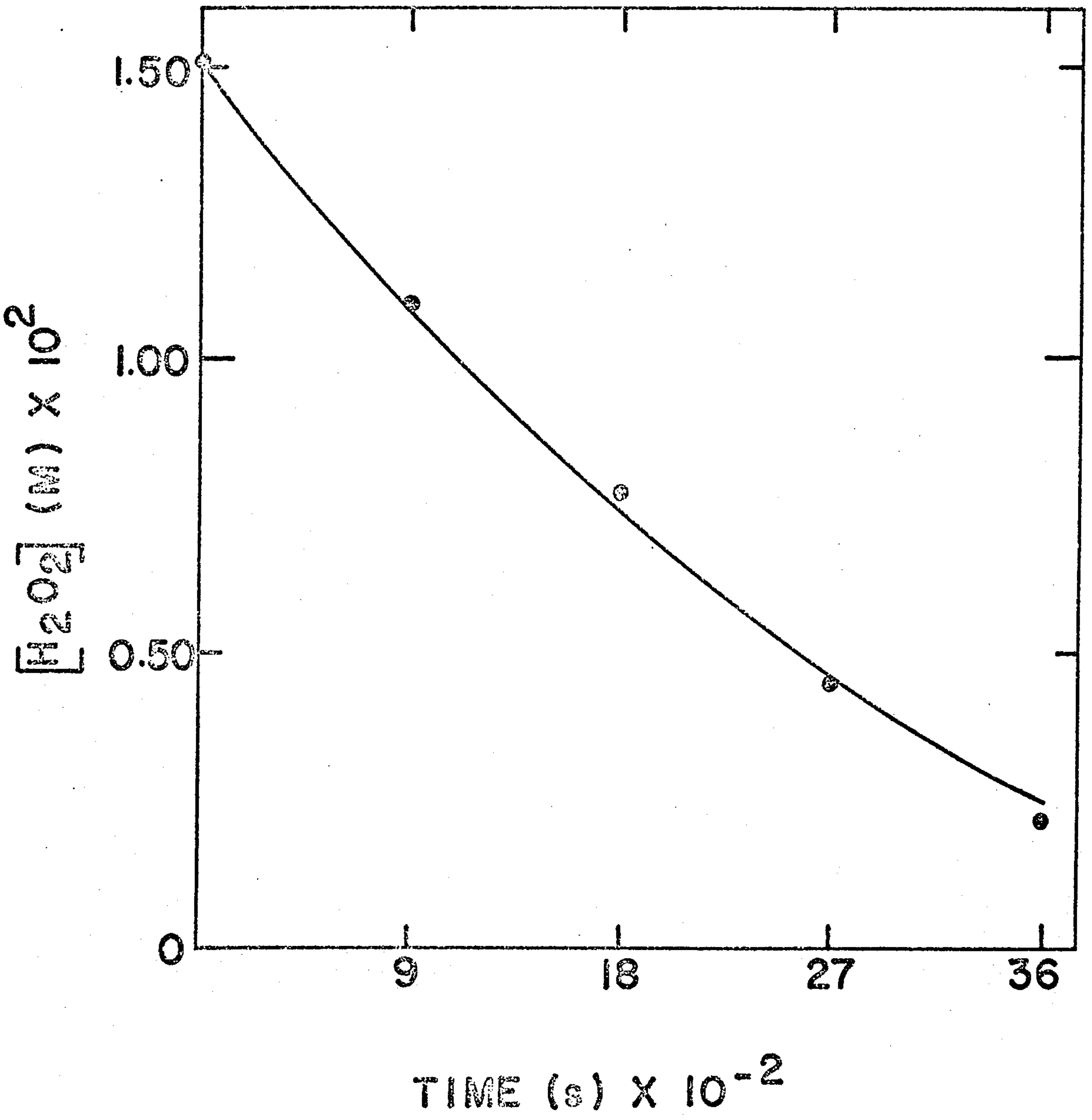
THF (M)	$G(-H_2O_2)$
0.12	28.0
0.37	27.5
0.62	23.8
0.87	30.0

Figure 3.3

A typical dose-yield plot for gamma-irradiated aqueous tetrahydrofuran containing H_2O_2.

[THF] = 0.124 M

Dose Rate = 9.18×10^{18} eV l^{-1} s^{-1}


1.50
1.00
0.50
0
9
18
27
36
$[H_2O_2]$ (M) x 10^2
TIME (s) X 10^{-2}

Changing the dose rate had no effect on the H_2O_2 removal yields as is displayed in Table 3.2. The initial concentrations of H_2O_2 and THF were 0.016 M H_2O_2 and 0.620 M THF.

TABLE 3.2

Variation of H_2O_2 Removal Yields with Dose Rate in Gamma-Irradiated Aqueous Solutions of THF

Dose Rate (eV l^{-1} s^{-1})	G ($-H_2O_2$)
7.78×10^{17}	32.7
2.57×10^{18}	35.6
9.28×10^{18}	33.5

3,3,4,4-d_4-Tetrahydrofuran/H_2O_2

The effect of deuterium substitution, at the 3 and the 4 positions in THF, on the H_2O_2 removal yields was studied. The opposite experiment, with deuterium substitution only at the 2 and the 5 positions in THF, was not attempted because 2,2,5,5-d_4-THF was not available.

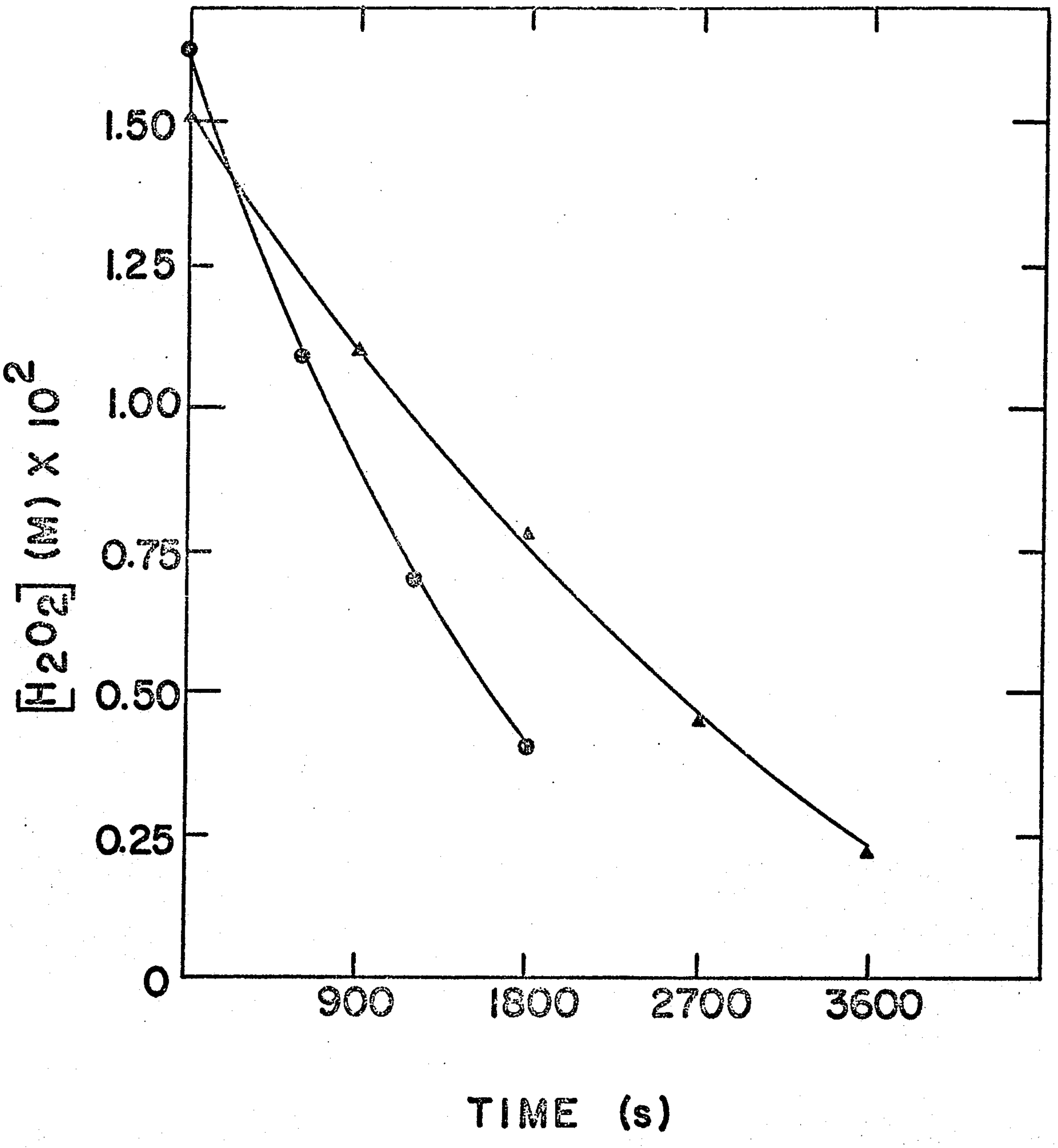
Although true competition experiments were not attempted, the dose-yield plots for the oxidation of THF were compared to those for 3,3,4,4-d_4-THF. As seen in Fig. 3.4, deuterium substitution at the 3 and the 4 positions increased

Figure 3.4

Gamma-radiation induced reduction of H_2O_2 by tetrahydrofuran and 3,3,4,4-d_4-tetrahydrofuran in aqueous solution.

●, $[3,3,4,4\text{-}d_4\text{-tetrahydrofuran}] = 0.124$ M
Dose Rate = 9.08×10^{18} eV l^{-1} s^{-1}

▲, $[\text{tetrahydrofuran}] = 0.124$ M
Dose Rate = 9.18×10^{18} eV l^{-1} s^{-1}



$[H_2O_2]$ (M) x 10^2
1.50
1.25
1.00
0.75
0.50
0.25
0
900
1800
2700
3600
TIME (s)

$G(-H_2O_2)$ from 29.9 to 59.2. The dose-yield plot for 3,3,4,4-d_4-THF remained independent of the H_2O_2 concentration, Fig. 3.5, and of the dose rate, Table 3.3. The initial concentrations of H_2O_2 and 3,3,4,4-d_4-tetrahydrofuran in the solutions used for the dose rate study were 0.032 M H_2O_2 and 0.12 M 3,3,4,4-d_4-tetrahydrofuran.

TABLE 3.3

Variation of the H_2O_2 Removal Yields with Dose Rate in Gamma-Irradiated Aqueous Solutions of 3,3,4,4-d_4-Tetrahydrofuran

Dose Rate (eV l^{-1} s^{-1})	$G(-H_2O_2)$
7.70×10^{17}	36.5
9.08×10^{18}	44.0

3.2 Discussion

The major features of the results are that the hydrogen peroxide removal yields are stoichiometrically equivalent to the 2-tetrahydrofuranol formation yields; independent of the hydrogen peroxide concentration, the tetrahydrofuran concentration and the dose rate. Furthermore, the substitution of 3,3,4,4-d_4-tetrahydrofuran for tetrahydrofuran results in a marked increase in the rate of the reaction.

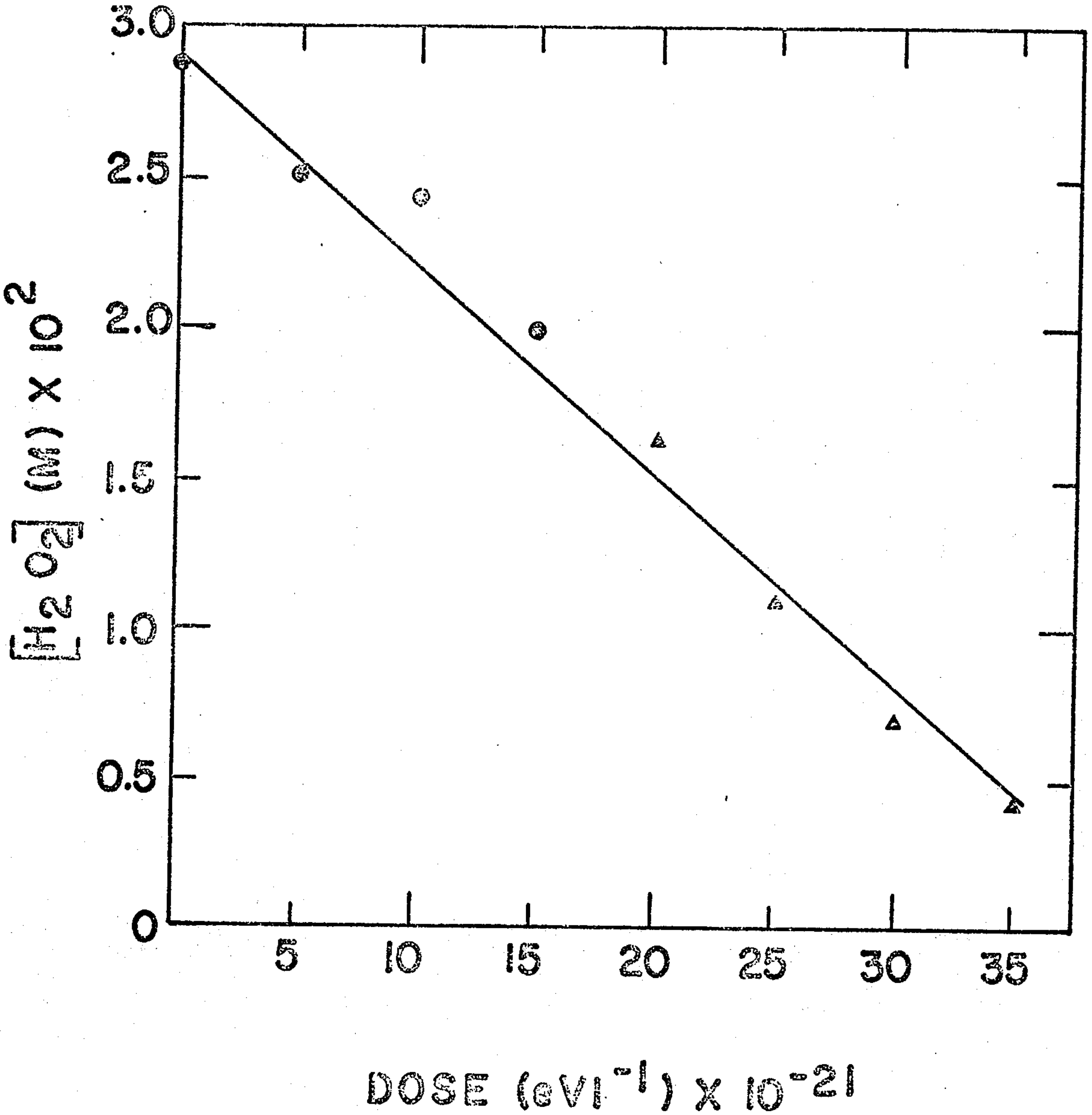
Figure 3.5

Gamma-radiation induced reduction of H_2O_2 in deuterated aqueous 0.124 M 3,3,4,4-d_4-tetrahydrofuran.

●, $[H_2O_2] = 2.87 \times 10^{-2}$ M

▲, $[H_2O_2] = 1.63 \times 10^{-2}$ M

Dose Rate = 9.08×10^{18} eV l^{-1} s^{-1}


3.0
2.5
2.0
1.5
1.0
0.5
0
5
10
15
20
25
30
35
[H2 O2] (M) X 10^2
DOSE (eVl^-1) X 10^-21

For these dilute aqueous solutions, the gamma-radiation interacts specifically with the bulk solvent.

$$(4)\quad H_2O \rightsquigarrow e^-_{aq},\ H,\ OH,\ H_3O^+,\ H_2O_2,\ H_2$$

The hydrated electron rapidly reacts with the solute, H_2O_2.

$$(5)\quad e^-_{aq} + H_2O_2 \longrightarrow OH + OH^-$$

Since $k_{OH + THF} \gg k_{OH + H_2O_2}$, $k_{H + THF} \approx k_{H + H_2O_2}$, and $[H_2O_2] \ll [THF]$, all of the H and OH radicals will react with THF. The H-atom abstraction from THF by OH and H radicals is probably not specific to the α-position.

Evidence for the abstraction of H from both the α- and the β-positions on THF by OH radicals is found in e.s.r. studies (11, 12, 16, 18) and in Fenton oxidation studies (9). Unfortunately, there is no evidence that H atoms abstract H from both positions on THF. However, it has been established that H-atom abstraction from secondary alcohols occurs significantly at the β-position (19,20). If H atoms are able to abstract H from a terminal methyl group, it is not unreasonable to expect that they can also do so from a methylene group. Therefore, reaction (23) is included in the reaction scheme.

$$(20)\quad OH + THF \longrightarrow II + H_2O$$

(21) $OH + THF \longrightarrow III + H_2O$

(22) $H + THF \longrightarrow II + H_2$

(23) $H + THF \longrightarrow III + H_2$

Only the α -radical is proposed to react with H_2O_2. In e.s.r. studies of THF oxidation by H_2O_2 (18), the spectrum of the β -radical was found to be enhanced by an increase in the H_2O_2 concentration. This phenomenon was interpreted as resulting from the preferential oxidation of the α -radical by H_2O_2. The propagating step is then given by reaction (24).

(24) $II + H_2O_2 \longrightarrow$ 2-tetrahydrofuranol + OH

The reactions terminates via a bimolecular reaction of the β -radicals, equation (25).

(25) $2\ III \longrightarrow$ termination products

This is somewhat simplistic and without an analysis of the termination products somewhat speculative, however, the nature of the results indicate it is a reasonable assumption. The two other possible termination reactions are given by equations (26) and (27).

(26) $2\ II \longrightarrow$ termination products

(27) $\mathrm{II} + \mathrm{III} \longrightarrow$ termination products

Bimolecular termination of α-radicals is highly unlikely at any H_2O_2 concentration, but cross-termination would increase at lower H_2O_2 concentrations. At lower H_2O_2 concentrations, the cross-termination reaction, eq. (27), would be in competition with the propagating reaction, eq. (24), resulting in some dependence of the reaction rate on the H_2O_2 concentration. The curvature of the dose-yield plot, Fig. 3.2, at lower H_2O_2 concentrations is evidence that such a termination is becoming more important at these H_2O_2 concentrations. Furthermore, the inclusion of a cross-termination reaction in the mechanism would lead to some dose rate dependence, but the effect would not be significant enough to be observed. A calculation of the relative contributions of each of these three termination reactions to the mechanism will be given in a later paragraph.

A radical conversion reaction, eq. (19),

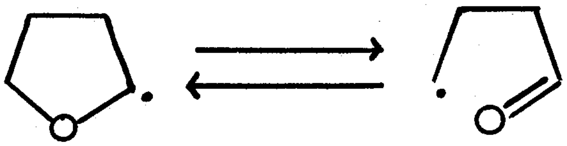
(19) $\mathrm{III} + \mathrm{THF} \longrightarrow \mathrm{II} + \mathrm{THF}$

similar to reaction (16) for 2-propanol or ethanol, is not likely. On energetic grounds, the probability of the 3-tetrahydrofuranyl radical abstracting a H-atom from the 2-position of THF is much less than that of the 1-(2-propanolyl) radical abstracting H from the 2-position on 2-propanol or the

2-ethanolyl radical abstracting H from the 1-position on ethanol.

The results, showing no dependence of the reaction on THF concentration, do not indicate a radical conversion reaction is occurring. Also, a ring opening reaction, eq. (28), is not needed to explain the results.

(28)



A ring opening, eq. (28), would compete with chain propagation, eq. (24), giving some dependence on H_2O_2 concentration; moreover, it would lead to a dose rate effect. Neither of these is seen at medium to high H_2O_2 concentrations.

The results may be accounted for by the mechanism summarized below.

(4) $H_2O \rightsquigarrow e^-_{aq}, H, OH, H_3O^+, H_2O_2, H_2$

(5) $e^-_{aq} + H_2O_2 \longrightarrow OH + OH^-$

(20) $OH + THF \longrightarrow II + H_2O$

(21) $OH + THF \longrightarrow III + H_2O$

(22) $H + THF \longrightarrow II + H_2$

(23) $H + THF \longrightarrow III + H_2$

(24) $II + H_2O_2 \longrightarrow$ 2-tetrahydrofuranol + OH

(25) $2\ III \longrightarrow$ termination products

Applying the usual steady state approximation to the above reaction scheme, the radiation chemical yield expression may be derived.

$$G(-H_2O_2) = G_{e^-_{aq}} - G_{H_2O_2} + \frac{k_{20}}{k_{21}}\left(G_{e^-_{aq}} + G_H + G_{OH}\right) + \left\{\frac{k_{22}}{k_{22}+k_{23}} - \frac{k_{20}}{k_{21}}\,\frac{k_{23}}{k_{22}+k_{23}}\right\}G_H \qquad (29)$$

This mechanism predicts a chain reaction with no dependence of the yields on the H_2O_2 concentration, the THF concentration, and the dose rate.

Assuming a value of 28.0 for $G(-H_2O_2)$ at zero THF concentration, the value of k_{20}/k_{21} may be estimated using the accepted values for the primary radical yields in irradiated water and the literature value for k_{22+23} (30). The values for k_{22} and k_{23} have not been reported for THF. The values for k_{22} and k_{23} were calculated by assuming the ratio k_{22}/k_{23} for THF would be approximately equal to the ratio k_{11}/k_{14} for ethanol.

$G_H + G_{e^-_{aq}} = 3.18$

$\frac{k_{22}}{k_{23}} = 9.14$ (30)

$G_{H_2O_2} = 0.68$

$G_{OH} = 2.72$ (31)

$k_{22+23} = 2.9 \times 10^7 M^{-1} s^{-1}$

$G_H = 0.55$ (32)

The value of k_{20}/k_{21} is calculated to be 5.6. This agrees with the values of the rate constant ratios found by Walling, El-Taliawi and Johnson (9) and by Gilbert, Norman and Sealy (11). Assuming k_{20+21} to be $1.6 \times 10^9 M^{-1} s^{-1}$ (30) allows the calculation of k_{20} and k_{21}.

$k_{20} = 0.24 \times 10^9 M^{-1} s^{-1}$

$k_{21} = 1.36 \times 10^9 M^{-1} s^{-1}$

The steady state value for the concentration ratio, $[\beta]/[\alpha]$, can be calculated using eq. (30).

$$(30)\quad [\beta]/[\alpha] = \frac{k_{21}}{k_{20}}\left\{1 + \frac{k_{24}[H_2O_2]}{(G_R D k_t)^{\frac{1}{2}}}\right\}$$

Assuming $2k_{25} = k_{26} = 2k_{27} = k_t = 2 \times 10^9\ M^{-1}\ s^{-1}$, $[\beta]/[\alpha]$ is 3.9 at a H_2O_2 concentration of 1.8×10^{-2} M and a dose rate of $8.5 \times 10^{18}\ eV\ l^{-1}\ s^{-1}$.

Using this value of $[\beta]/[\alpha]$, the percent relative contribution of reactions (26), (27), and (25) to the termination of the chain reaction is calculated to be 4, 32, and 64%. As the H_2O_2 concentration decreases, reaction (27) becomes more important as a termination pathway, leading to some dependence of the yields on the H_2O_2 concentration. Such an occurance would manifest itself as a curvature in the dose-yield plot at a constant THF concentration. In Fig. 3.1, the plot does not significantly curve, however, this was found to be due to some peroxide impurity in the THF. The two higher concentrations of H_2O_2 were run with purified THF and the curve is seen at 1.00×10^{-2} M H_2O_2, Fig. 3.2.

When 3,3,4,4-d_4-THF is substituted for THF, reactions (21) and (23) should show a normal primary kinetic isotope effect if they are H atom transfer reactions.

Equation (29) predicts an increase in $G(-H_2O_2)$ with a decrease in the rate constant ratio for H atom abstraction from the β-position by the OH radical. This was found experimentally as k_{20}/k_{21} increased from 5.6 for THF to 9.5 for 3,3,4,4-d_4-THF, Fig. 3.4. Similarly, if 2,2,5,5-d_4-THF were substituted for THF, a normal primary kinetic isotope effect should be shown by reactions (20) and (22). This should result in a decrease of $G(-H_2O_2)$ if eq. (29) is valid.

Assuming secondary isotope effects are insignificant, the rate constant ratio, $k_{21(H)}/k_{21(D)}$, is calculated to be 1.7. This value is comparable with the value found for 2-propanol, 1.4 (33, 34), and for ethanol, 1.2 (33).

The proposed mechanism for the gamma-radiation induced oxidation of THF by H_2O_2 in dilute aqueous solutions accounts for all the experimental results. It appears self-consistent and in agreement with previously reported research. It was anticipated that the kinetics of the oxidation of 1,4-dioxane would be different since only one radical derived from 1,4-dioxane by H-atom abstraction was expected.

4. RESULTS AND DISCUSSION - 1,4-DIOXANE AND 1,3-DIOXOLANE

4.1 Results

The gamma-radiation induced oxidation of 1,4-dioxane and 1,3-dioxolane, in deaerated aqueous solutions, by hydrogen peroxide was investigated over a range of hydrogen peroxide concentrations, ether concentrations, and dose rates. For 1,4-dioxane, the effect of deuterium substitution was also studied. The results of these experiments are presented and discussed in the following sections.

1,4-Dioxane/H_2O_2

The hydrogen peroxide removal yields in the presence of a constant concentration of 1,4-dioxane (0.590 M) are shown in a dose-yield plot, Fig. 4.1. The graph is a composite figure constructed by combining the dose-yield results for three different initial concentrations of hydrogen peroxide. The hydrogen peroxide removal yields for a constant ether concentration are independent of peroxide concentration over the range 3×10^{-2} M to 5×10^{-3} M H_2O_2. The curved plots in Fig. 4.2 demonstrate that the expected first-order kinetics were not observed.

All dose-yield plots for peroxide removal are linear over the half-life of the reaction allowing accurate

Figure 4.1

Gamma-radiation induced reduction of H_2O_2 in deaerated aqueous 0.590 M 1,4-dioxane.

Dose Rate = 10.58×10^{18} eV l^{-1} s^{-1}

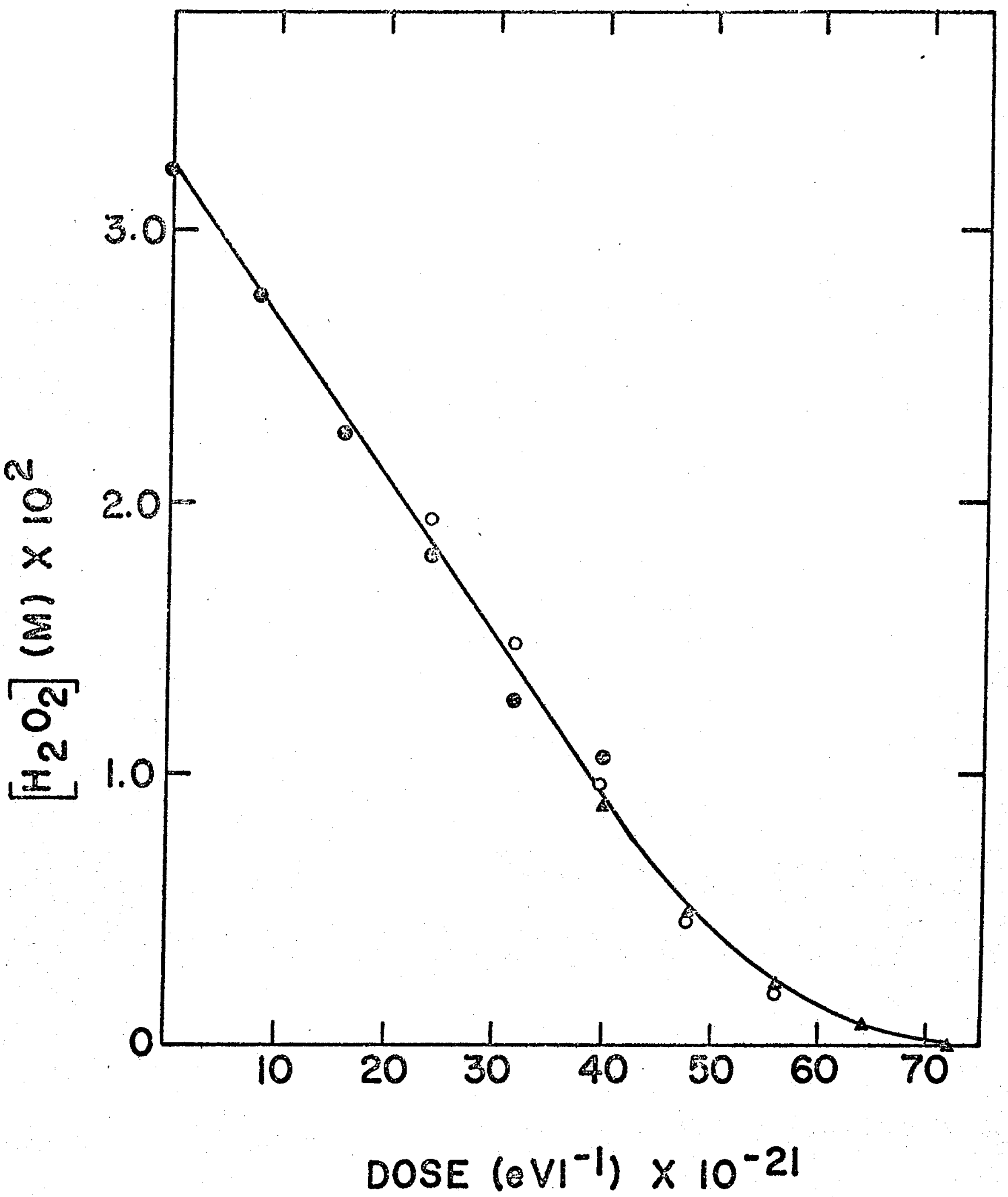
$[H_2O_2]$ =

● ,0.032 M

○ ,0.018 M

▲ ,0.009 M

For each symbol, the initial point on the graph represents zero dose.



$[H_2O_2]$ (M) X 10^2
3.0
2.0
1.0
0
10
20
30
40
50
60
70
DOSE (eVl^{-1}) X 10^{-21}

Figure 4.2

First order plots for H_2O_2 reduction in gamma-irradiated solutions of 1,4-dioxane.

Dose Rate = 10.58×10^{18} eV l^{-1} s^{-1}

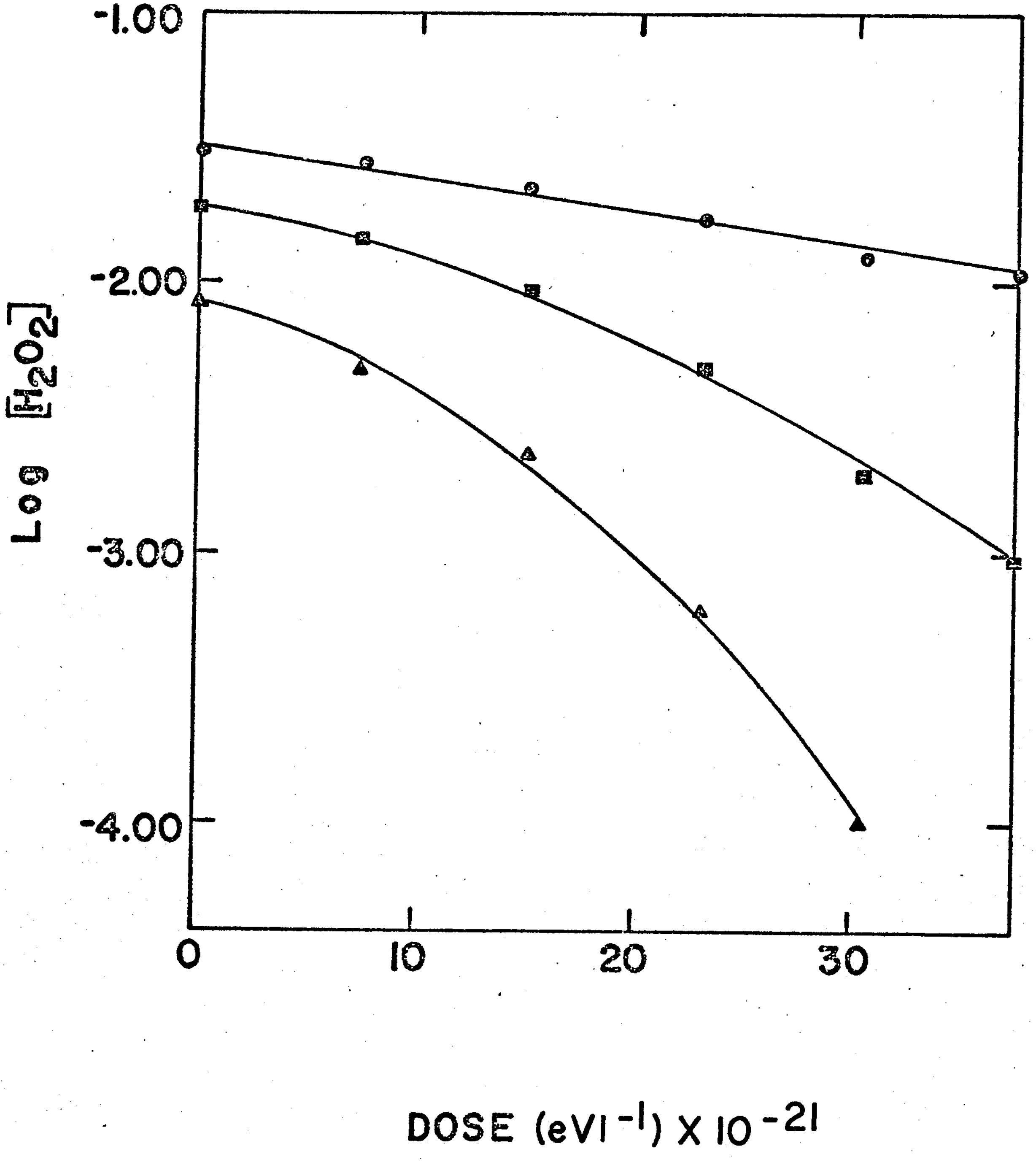
[1,4-dioxane] = 0.590 M

$[H_2O_2]$ =

● ,0.032 M

■ ,0.018 M

▲ ,0.009 M


-1.00
-2.00
-3.00
-4.00
Log $[H_2O_2]$
0
10
20
30
DOSE (eVl⁻¹) X 10⁻²¹

calculation of $G(-H_2O_2)$ values. A typical dose-yield plot for hydrogen peroxide removal is shown in Fig. 4.3. The curvature of the graph towards the end of the reaction was characteristic of all the dose-yield plots. The stoichiometry of the reaction was determined only at a single value of the absorbed dose because of the tediousness of the analysis. At 18.8×10^{21} eV l^{-1}, the hydrogen peroxide removal yield, $G(-H_2O_2) = 30.9 \pm 0.2$, was equivalent to the 1,4-dioxan-2-ol formation yield, G(1,4-dioxan-2-ol) = 30.0 ± 0.9.

The hydrogen peroxide removal yields are independent of the ether concentration. This is illustrated in Table 4.1. The initial H_2O_2 concentration is 0.018 M H_2O_2 and the dose rate is 10.58×10^{18} eV l^{-1} s^{-1}.

TABLE 4.1

Variation of H_2O_2 Removal Yields with 1,4-Dioxane Concentration

1,4-Dioxane (M)	$G(-H_2O_2)$
0.12	39.4
0.35	41.5
0.59	39.6
0.83	42.4

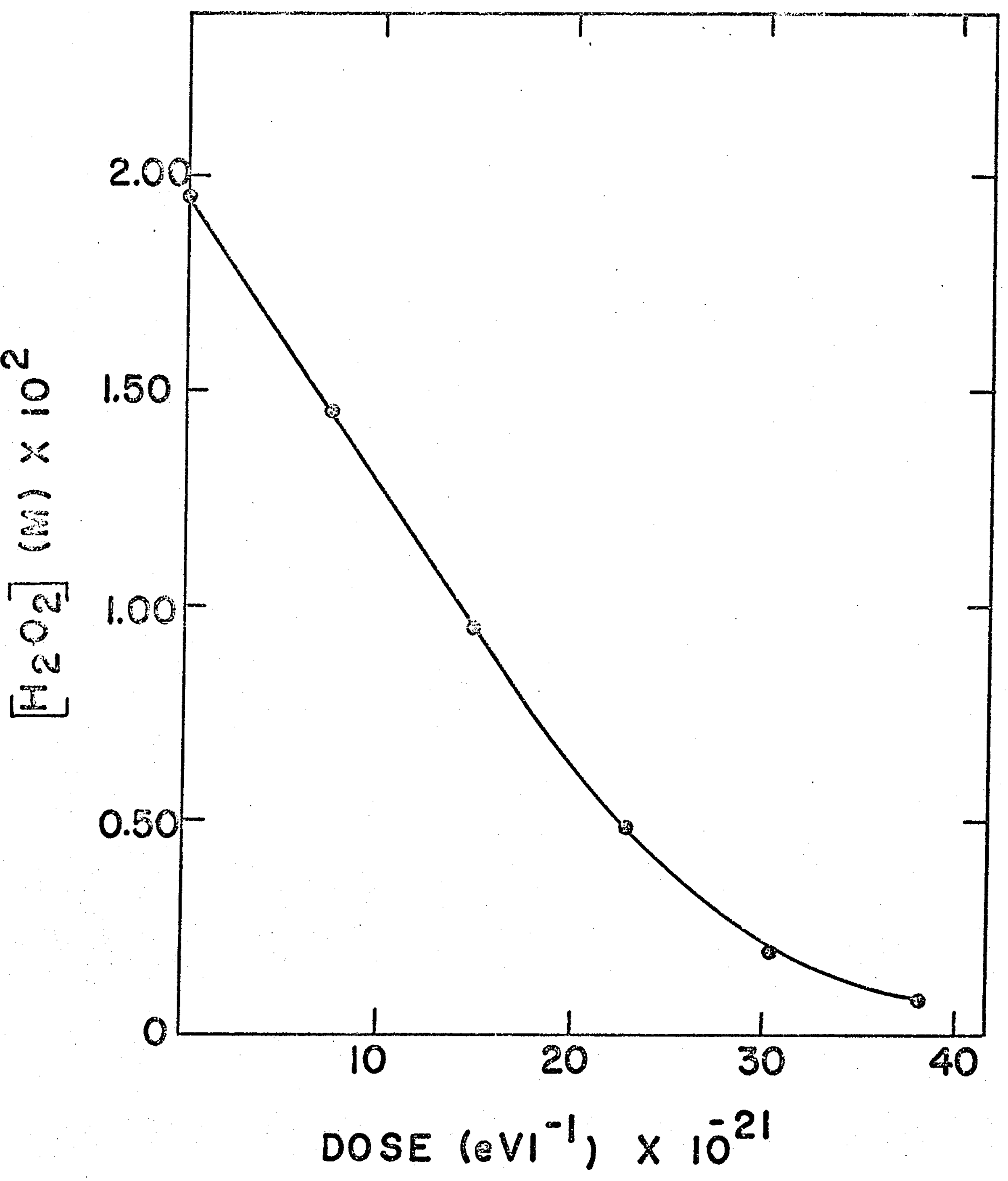
The effect of dose rate on peroxide removal

Figure 4.3

A typical dose-yield plot for gamma-irradiated aqueous 1,4-dioxane containing H_2O_2.

$[\text{1,4-dioxane}] = 0.590$ M

Dose Rate = 10.58×10^{18} eV l^{-1} s^{-1}


2.00
1.50
1.00
0.50
0
10
20
30
40
$[H_2O_2]$ (M) x 10^2
DOSE (eVl^{-1}) x 10^{-21}

yields is displayed in Table 4.2, where the initial concentrations of H_2O_2 and 1,4-dioxane are 0.018 M H_2O_2 and 0.590 M 1,4-dioxane. The hydrogen peroxide removal yields are independent of the dose rate.

TABLE 4.2

Variation of H_2O_2 Removal Yields with Dose Rate in Gamma-Irradiated Solutions of 1,4-Dioxane

Dose Rate (eV l^{-1} s^{-1})	$G(-H_2O_2)$
7.78×10^{17}	43.0
2.54×10^{18}	41.3
9.28×10^{18}	39.6

2,2,3,3,5,5,6,6-d_8-1,4-Dioxane/H_2O_2

When the reaction was tried with 2,2,3,3,5,5,6,6-d_8-1,4-dioxane, the hydrogen peroxide removal yields remained independent of the hydrogen peroxide concentration, Fig. 4.4, and of the dose rate, Table 4.3. The initial concentrations of H_2O_2 and 2,2,3,3,5,5,6,6-d_8-1,4-dioxane in the solutions and for the dose rate studies are 0.032 M H_2O_2 and 0.118 M 2,2,3,3,5,5,6,6-d_8-1,4-dioxane.

Figure 4.4

Gamma-radiation induced reduction of H_2O_2 in deaerated aqueous 0.590 M 2,2,3,3,5,5,6,6-d_8-1,4-dioxane.

Dose Rate = 9.08×10^{18} eV l^{-1} s^{-1}

$[H_2O_2]$ =

● ,0.032 M

▲ ,0.016 M

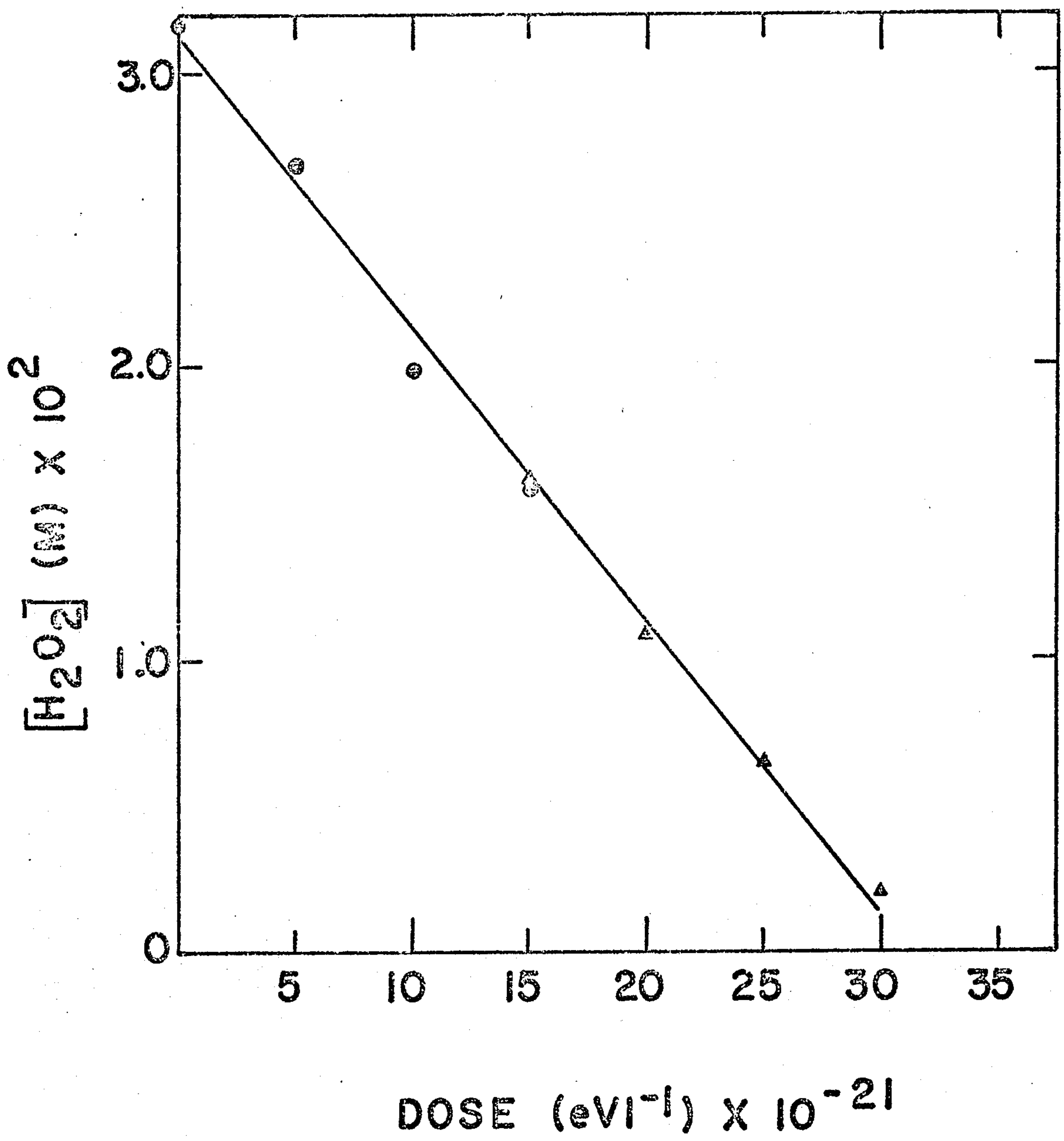

3.0
2.0
1.0
0
5
10
15
20
25
30
35
$[H_2O_2]$ (M) x 10^2
DOSE (eVl^{-1}) X 10^{-21}

TABLE 4.3

Variation of the H_2O_2 Removal Yields with Dose Rate in Gamma-Irradiated Aqueous Solutions of 2,2,3,3,5,5,6,6-d_8-1,4-Dioxane

Dose Rate (eV l^{-1} s^{-1})	G($-H_2O_2$)
7.70×10^{17}	36.5
9.08×10^{18}	29.0

The effect of the ether concentration on the reaction rate was not checked.

As depicted in Fig. 4.5, the deuterium substitution did not affect the rate of the reaction.

1,3-Dioxolane/H_2O_2

The only major observable different between the oxidation of 1,3-dioxolane and the oxidation of either THF or 1,4-dioxane was the much larger G($-H_2O_2$) values for the former solute.

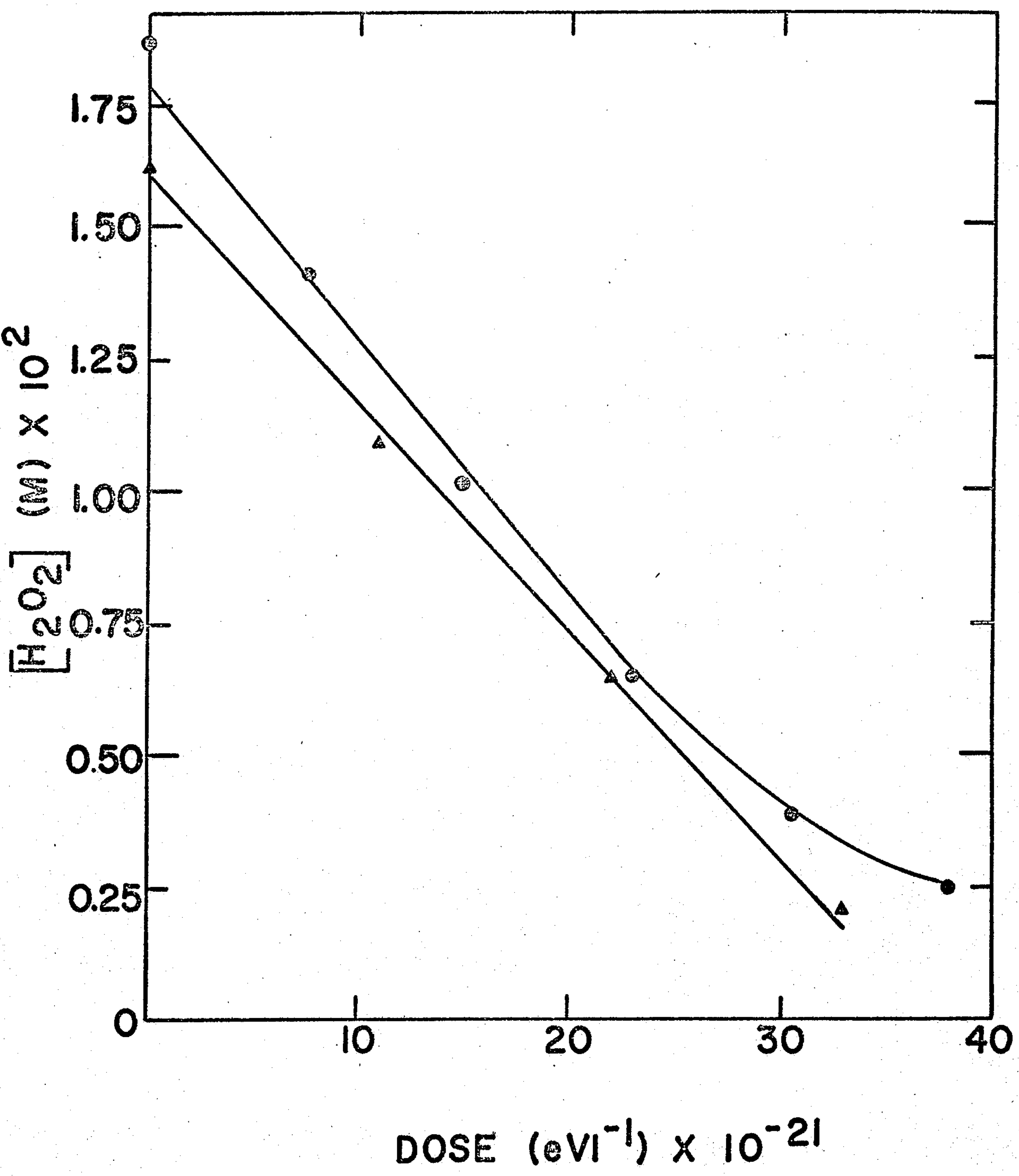
The stoichiometry of the reaction was not determined because a method of synthesizing either 1,3-dioxolan-2-ol or 1,3-dioxolan-4-ol, the two probable major products, could not be found. The difficulty of the product analysis would be aggravated if these two products underwent ring

Figure 4.5

Gamma-radiation induced reduction of H_2O_2 by 1,4-dioxane and 2,2,3,3,5,5,6,6-d_8-1,4-dioxane in aqueous solution.

● , [1,4-dioxane] = 0.118 M
Dose Rate = 9.28 x 10^{18} eV l^{-1} s^{-1}

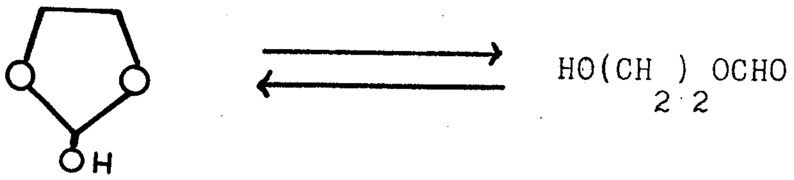
▲ , [2,2,3,3,5,5,6,6-d_8-1,4-dioxane] = 0.118 M
Dose Rate = 9.08 x 10^{18} eV l^{-1} s^{-1}



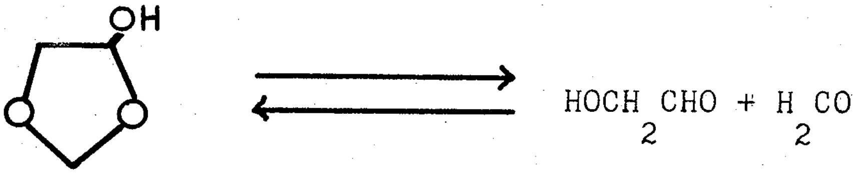
$[H_2O_2]$ (M) × 10^2
1.75
1.50
1.25
1.00
0.75
0.50
0.25
0
10
20
30
40
DOSE (eVl^{-1}) × 10^{-21}

opening in aqueous solutions, eq. (31) and eq. (32), as proposed by Meerwein et al (25).

(31)



(32)



The H_2O_2 removal yields were measured as a function of the dose, and a typical dose-yield plot at a 1,3-dioxolane concentration of 0.715 M and a H_2O_2 concentration of 1.62×10^{-2} M is depicted in Fig. 4.6. The values of $G(-H_2O_2)$ were calculated using the initial slopes of the curves. For the dose-yield plot in Fig. 4.6, $G(-H_2O_2)$ was determined to be 82.0.

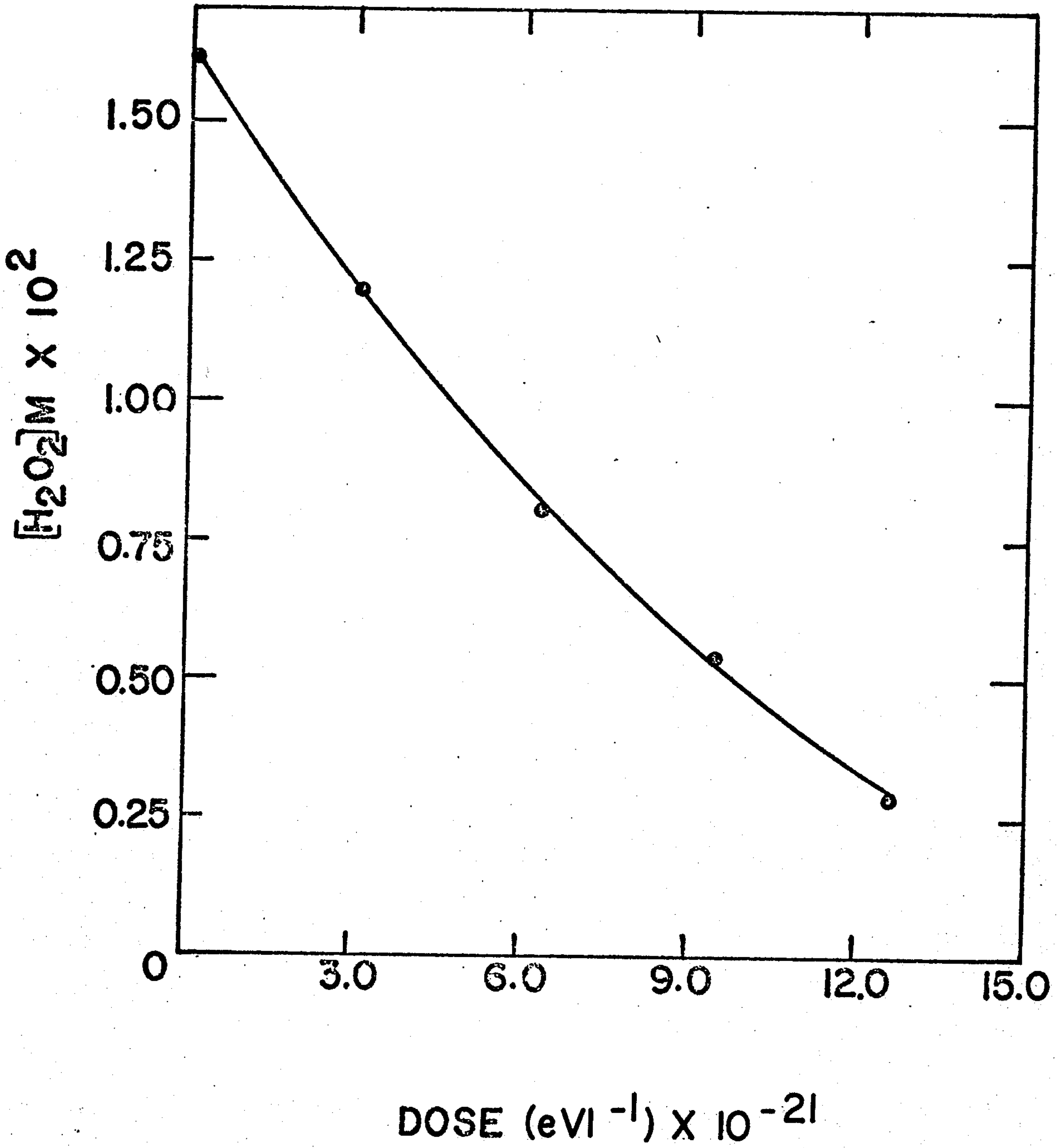
The dose-yield plots for the H_2O_2 removal yields, at a constant 1,3-dioxolane concentration of 0.715 M, are illustrated in Fig. 4.7. The curve was constructed, as for the THF and the 1,4-dioxane experiments, from dose-yield plots for three different initial H_2O_2 concentrations. The H_2O_2 removal yields are independent of the H_2O_2 concentration over

Figure 4.6

A typical dose-yield plot for gamma-irradiated aqueous 1,3-dioxolane containing H_2O_2.

$[\text{1,3-dioxolane}] = 0.715$ M

Dose Rate = 10.47×10^{18} eV l^{-1} s^{-1}



$[H_2O_2]M \times 10^2$
1.50
1.25
1.00
0.75
0.50
0.25
0
3.0
6.0
9.0
12.0
15.0
DOSE $(eVl^{-1}) \times 10^{-21}$

Figure 4.7

Gamma-radiation induced reduction of H_2O_2 in deaerated aqueous 0.715 M 1,3-dioxolane.

Dose Rate = 10.35×10^{18} eV l^{-1} s^{-1}

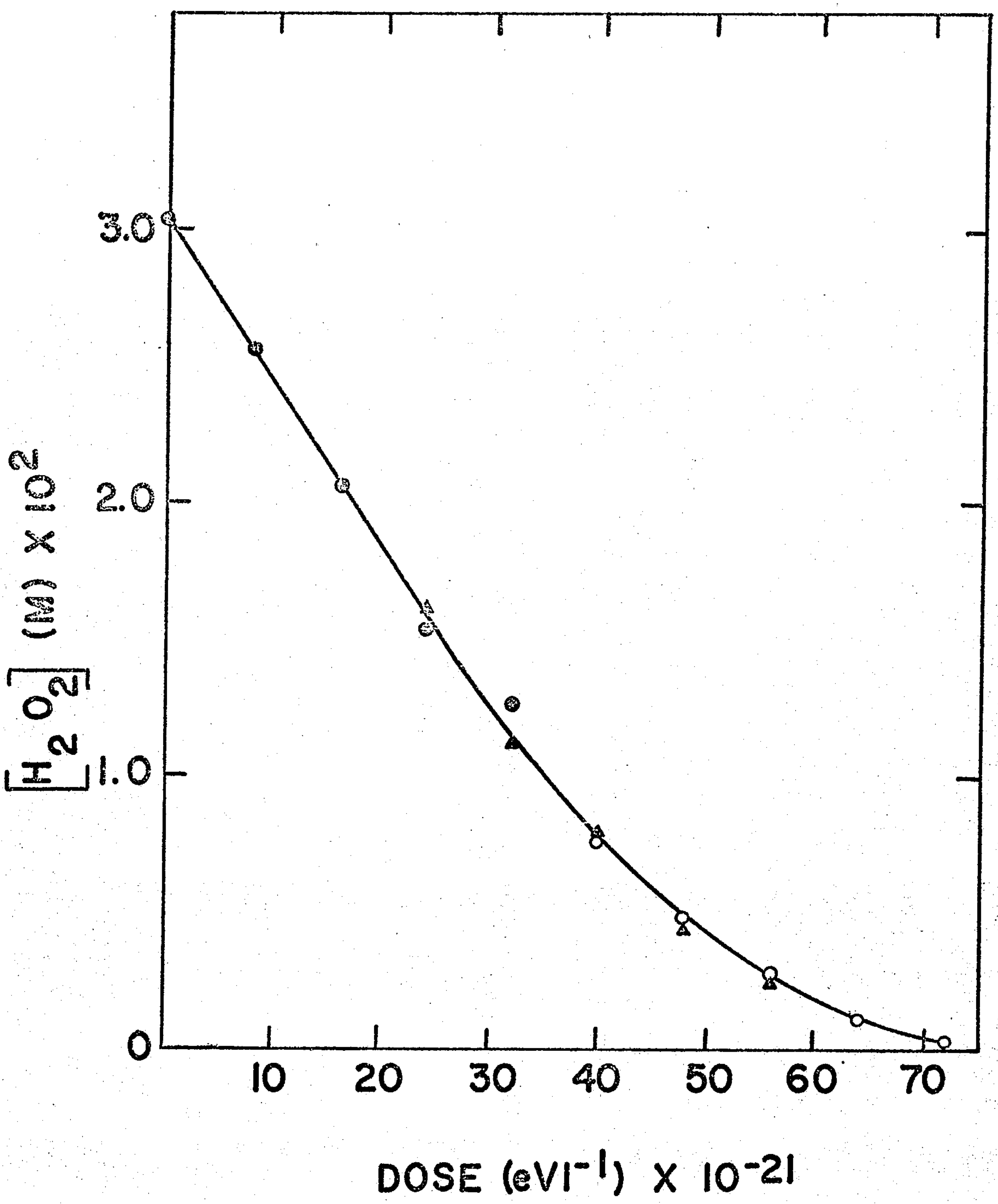
$[H_2O_2]$ =

● ,0.031 M

▲ ,0.016 M

○ ,0.008 M

For each symbol, the initial point on the graph represents zero dose.


3.0
2.0
1.0
0
10
20
30
40
50
60
70
$[H_2O_2]$ (M) X 10^2
DOSE (eVl^{-1}) X 10^{-21}

the range 0.77 x 10^{-2} M to 3.04 x 10^{-2} M H_2O_2. At concentrations lower than 0.80 x 10^{-2} M H_2O_2, the slope of the curve indicates that the H_2O_2 concentration becomes an increasingly important factor.

Table 4.4 shows that the H_2O_2 removal yields are independent of the 1,3-dioxolane concentration over the range 0.143 M to 1.001 M 1,3-dioxolane. The initial H_2O_2 concentration is 0.016 M H_2O_2 and the dose rate is 10.35 x 10^{18} eV l^{-1} s^{-1}.

TABLE 4.4

Variation of H_2O_2 Removal Yields with 1,3-Dioxolane Concentration

1,3-Dioxolane (M)	G(-H_2O_2)
0.14	73.0
0.43	74.5
0.71	77.9
1.00	73.0

The results of the dose rate studies are illustrated in Table 4.5, where the initial concentrations of H_2O_2 and 1,3-dioxolane are 0.016 M H_2O_2 and 0.715 M 1,3-dioxolane. Although the H_2O_2 yields are not clearly independent of the dose rate, the relationship is not a simple one.

TABLE 4.5

Variation of H_2O_2 Removal Yields with Dose Rate in Gamma-Irradiated Aqueous Solutions of 1,3-Dioxolane

Dose Rate ($eV\ l^{-1}\ s^{-1}$)	$G(-H_2O_2)$
7.70×10^{17}	130.2
2.75×10^{18}	93.2
10.13×10^{18}	83.6

4.2 Discussion

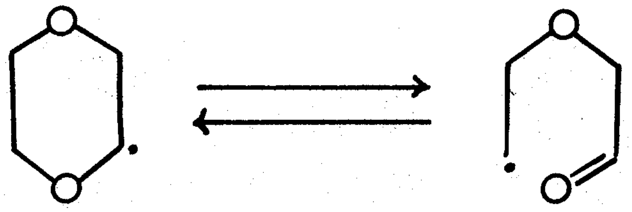
1,4-Dioxane

Some of the results for the oxidation of dioxane were unexpected and quite puzzling. As predicted, the H_2O_2 removal yields were stoichiometrically equivalent to the 1,4-dioxan-2-ol formation-yields, independent of the THF concentration and unaffected by deuterium substitution. The fact that the H_2O_2 removal yields were independent of both the H_2O_2 concentration and the dose rate was unexpected. A mechanism to account for all the results was not found.

Because 1,4-dioxane can give rise to only one type of radical, it was expected that its oxidation by H_2O_2 would follow a mechanism similar to that proposed for methanol, eq. (4) - (9). Equation (10) predicts a first order dependence on H_2O_2 and a square root dependence on dose rate. This mechanism does not account for the experimental results found for 1,4-dioxane.

The possibility of a ring opening, eq. (33), which would yield a product that could take part only in termination, eq. (34), was considered.

(33)



IX

(34) 2 IX ⟶ termination products

Although this would account for the lack of a dose rate effect because there would be no competition between reaction (8) and reaction (9), it introduces a competition between reaction (33) and reaction (8), which would result in a first order dependence on H_2O_2. It was not necessary to invoke ring opening to explain the THF result, and it would be reasonable to assume that if 1,4-dioxane underwent ring opening the same would apply to THF. Any form of ring opening was therefore discounted for 1,4-dioxane and the results are left unexplained.

All e.s.r. studies of the oxidation of 1,4-dioxane show only one radical is formed, the 1,4-dioxanyl radical, and that this radical can undergo oxidation by H_2O_2. The results show 1,4-dioxan-2-ol was formed in stoichiometric equivalents to the H_2O_2 removal so that reaction (35) is probably the propagating reaction.

$$(35) \quad I + H_2O_2 \longrightarrow \text{1,4-dioxan-2-ol} + OH$$

No explanation for the lack of a H_2O_2 concentration and a dose rate dependence can be given.

1,3-Dioxolane

A meaningful mechanism for the gamma-radiation induced oxidation of 1,3-dioxolane by hydrogen peroxide cannot be proposed because the reaction products were not identified. Any mechanism proposed would have to account for the lack of dependence of the yields on peroxide concentration, 1,3-dioxolane concentration and dose rate.

The following mechanism, similar to the one for the oxidation of THF is a possibility.

$$(4) \quad H_2O \rightsquigarrow e^-_{aq}, H, OH, H_3O^+, H_2O_2, H_2$$

(5) $e^-_{aq} + H_2O_2 \longrightarrow OH + OH^-$

(36) $OH + \text{1,3-dioxolane} \longrightarrow IV + H_2O$

(37) $H + \text{1,3-dioxolane} \longrightarrow IV + H_2$

(38) $OH + \text{1,3-dioxolane} \longrightarrow V + H_2O$

(39) $H + \text{1,3-dioxolane} \longrightarrow V + H_2$

(40) $IV + H_2O_2 \longrightarrow$ molecular products + OH

(41) $2\ V \longrightarrow$ termination products

Such a mechanism does explain the experimental results, however, the assumption that the 4-(1,3-dioxolanyl) radical does not undergo oxidation by H_2O_2 is not experimentally justified.

Gilbert, Norman and Sealy (11) found the ratio k_{34}/k_{36} to be 0.47 for 1,3-dioxolane at an initial H_2O_2 concentration of 5×10^{-2} M H_2O_2. This would mean $G(-H_2O_2)$ should be about 5 if the above mechanism, eq. (4), (5), (36-41), were valid. Experimentally, $G(-H_2O_2)$ was found to be about 70, which would yield, using eq. (29), a k_{34}/k_{36} ratio of 13.

5. CONCLUSION

Some of the results of this investigation do not fulfill the initial expectations. A mechanism could be proposed for the oxidation of only one of the ethers. The two-radical mechanism proposed for THF appears to be valid but could not be confirmed with the results for 1,4-dioxane. No further experiment to clarify the results for 1,4-dioxane could be conceived. Further work is necessary to characterize the mechanism of the gamma-radiation induced oxidation of 1,4-dioxane and 1,3-dioxolane by hydrogen peroxide in dilute aqueous solutions.

APPENDIX A

LIST OF EQUATIONS

1. $I + H_2O_2 \longrightarrow$ molecular products $+ OH$

2. $II + H_2O_2 \longrightarrow$ molecular products $+ OH$

3. $IV + H_2O_2 \longrightarrow$ molecular products $+ OH$

4. $H_2O \rightsquigarrow e^-_{aq},\ H,\ OH,\ H_3O^+,\ H_2O_2,\ H_2$

5. $e^-_{aq} + H_2O_2 \longrightarrow OH + OH^-$

6. $H + CH_3OH \longrightarrow H_2 + \cdot CH_2OH$

7. $OH + CH_3OH \longrightarrow H_2O + VII$

8. $VII + H_2O_2 \longrightarrow HCHO + H_2O + OH$

9. $2\ VII \longrightarrow$ termination products

10. $$-\frac{d\left[H_2O_2\right]}{dt} = (G_{e^-_{aq}} - G_{H_2O_2})\,D + k_8\left[\frac{(G_{e^-_{aq}} + G_H + G_{OH})\,D}{2k_9}\right]^{\frac{1}{2}}\left[H_2O_2\right]$$

11. $H + (CH_3)_2CHOH \longrightarrow H_2 + (CH_3)_2\dot{C}OH$

12. $OH + (CH_3)_2CHOH \longrightarrow H_2O + IV$

13. $VI + H_2O_2 \longrightarrow (CH_3)_2CO + OH + H_2O$

APPENDIX A

LIST OF EQUATIONS

14. $H + (CH_3)_2CHOH \longrightarrow H_2 + \cdot CH_2CH_3CHOH$

15. $OH + (CH_3)_2CHOH \longrightarrow H_2O + VIII$

16. $VIII + (CH_3)_2CHOH \longrightarrow VI + (CH_3)_2CHOH$

17. $2\ VIII \longrightarrow$ termination products

18. $$G(-H_2O_2) = G_{e^-_{aq}} - G_{H_2O_2} + G_H\left\{\frac{k_{11}(k_{12} + k_{15})}{k_{15}(k_{11} + k_{14})}\right\} + \frac{k_{12}}{k_{13}}\left(G_{e^-_{aq}} + G_{OH}\right) + 1 + \frac{k_{12}}{k_{13}}k_{16}\left\{\frac{G_{e^-_{aq}} + G_H + G_{OH}}{ak_{17}D}\right\}^{\frac{1}{2}}$$

$[2\text{-propanol}]$

19. $III + THF \longrightarrow II + THF$

20. $OH + THF \longrightarrow II + H_2O$

21. $OH + THF \longrightarrow III + H_2O$

22. $H + THF \longrightarrow II + H_2$

23. $H + THF \longrightarrow III + H_2$

APPENDIX A

LIST OF EQUATIONS

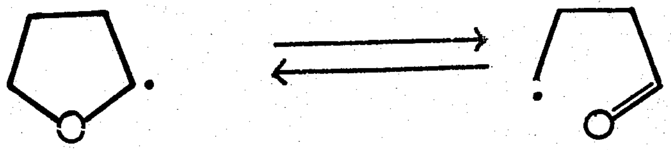
24. $\mathrm{II} + H_2O_2 \longrightarrow$ 2-tetrahydrofuranol + OH

25. $2\ \mathrm{III} \longrightarrow$ termination products

26. $2\ \mathrm{II} \longrightarrow$ termination products

27. $\mathrm{II} + \mathrm{III} \longrightarrow$ termination products

28.



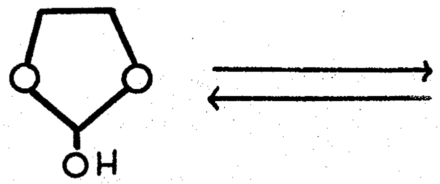
29. $$G(-H_2O_2) = G_{e^-_{aq}} - G_{H_2O_2} + \frac{k_{20}}{k_{21}}\left(G_{e^-_{aq}} + G_H + G_{OH}\right) + \left\{\frac{k_{22}}{k_{22}+k_{23}} - \frac{k_{20}}{k_{21}}\ \frac{k_{23}}{k_{22}+k_{23}}\right\} G_H$$

30. $$[\beta]/[\alpha] = \frac{k_{21}}{k_{20}}\left\{1 + \frac{k_{24}\ H_2O_2}{(G_R\ D\ k_t)^{\frac{1}{2}}}\right\}$$

APPENDIX A

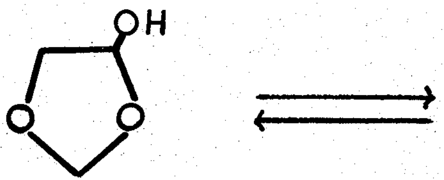
LIST OF EQUATIONS

31.



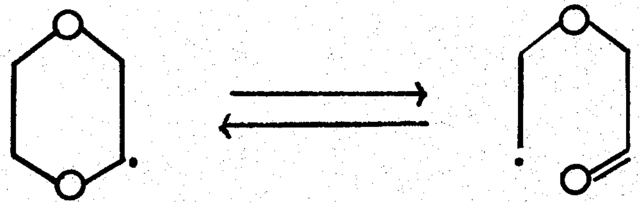
$HO(CH_2)_2OCHO$

32.



$HOCH_2CHO + H_2CO$

33.



34. 2 IX → termination products

35. I + H_2O_2 → 1,4-dioxan-2-ol + OH

36. OH + 1,3-dioxolane → IV + H_2O

APPENDIX A

LIST OF EQUATIONS

37. $H + 1,3\text{-dioxolane} \longrightarrow IV + H_2$

38. $OH + 1,3\text{-dioxolane} \longrightarrow V + H_2O$

39. $H + 1,3\text{-dioxolane} \longrightarrow V + H_2$

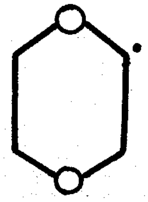
40. $IV + H_2O_2 \longrightarrow \text{molecular products} + OH$

41. $2V \longrightarrow \text{termination products}$

APPENDIX B

LIST OF RADICALS

I =



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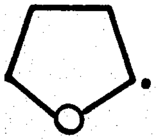

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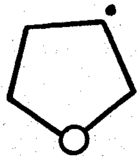

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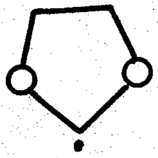

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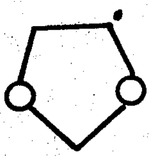

APPENDIX B

LIST OF RADICALS

VI = $(CH_3)_2\dot{C}OH$

VII = $\cdot CH_2OH$

VIII = $\cdot CH_2CH_3CHOH$

IX = $\dot{C}H_2CH_2OCH_2CHO$

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