

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  $\text{H}_2\text{O}_2$  in neutral solutions has been investigated. Tetrahydrofuran and 1,4-dioxane are oxidized to 2-tetrahydrofuranol and 1,4-dioxan-2-ol and the  $\text{H}_2\text{O}_2$  is reduced in stoichiometrically equivalent yields. For all three ethers, the yields are independent of the ether concentration, the  $\text{H}_2\text{O}_2$  concentration and the dose rate. Substitution of 3,3,4,4-d<sub>4</sub>-tetrahydrofuran for tetrahydrofuran results in increased yields, while substitution of 2,2,3,3,5,5,6,6-d<sub>8</sub>-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  $\text{H}_2\text{O}_2$  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<sub>2</sub>O<sub>2</sub> 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<sub>2</sub>O<sub>2</sub> 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<sub>2</sub>O<sub>2</sub> 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  $\alpha$ -radicals analogous to those from methanol. An  $\alpha$ -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  $\alpha$ -radical and a  $\beta$ -radical. A  $\beta$ -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  $\beta$ -radical, can form two different types of  $\alpha$ -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 pre-

dominately 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:  $H$ ,  $OH$ ,  $e^-$ ,  $H_2O_{aq}$ ,  $H_2$ ,  $H_2O_2$ . 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 electronvolts 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 ( $G D$  or  $G(x)D$ ) is the concentration of x formed per unit time.  
x

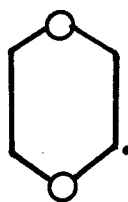
### 1.3 Related Studies

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).

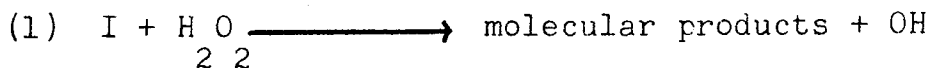
Walling, El-Taliawi and Johnson (9), using Fenton's reagent to generate radicals, studied the oxidation of 1,4-dioxane and THF by  $H_2O_2$ . The results were explained by mechanisms in which 1,4-dioxane yielded one radical species, easily oxidized by  $H_2O_2$  and  $Fe^{3+}$ , while THF yielded two 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  $\alpha$ -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  $\text{Ti(III)-H}_2\text{O}_2$  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  $\text{H}_2\text{O}_2$ ,  $k_{11}$ , was calculated to be  $1.0 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ .

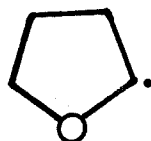


I

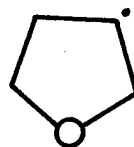


Oxidation of THF gave two radicals, previously

identified as II and III (12, 16), in an initial radical concentration ratio,  $[II] / [III]$  of 6.0.



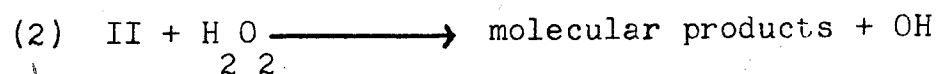
II



III

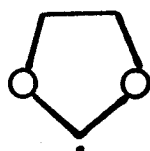
Increasing the  $Ti(III)$  concentration, at a constant  $H_2O_2$  concentration, resulted in an increase in the radical concentration ratio,  $[II] / [III]$ .

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

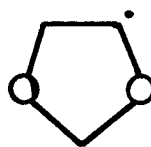


Two previously identified radicals, IV and V (16, 17), were observed for 1,3-dioxolane. The initial radical concentration ratio,  $[III] / [II]$ , was 1.18 at a  $H_2O_2$  concentration of  $3.5 \times 10^{-3} \text{ M}$ , and increased to 2.15 at a  $H_2O_2$  concentration of  $5 \times 10^{-2} \text{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



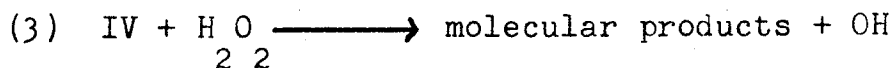


IV

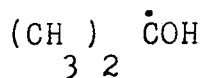


V

Assuming the preferential oxidation of IV at a very low  $\text{H}_2\text{O}_2$  concentration, the rate constant for the reaction of IV with  $\text{H}_2\text{O}_2$ ,  $k_{(3)}$ , was estimated to be  $6 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ . This value should be regarded as a lower limit.



The preferential oxidation of II by  $\text{H}_2\text{O}_2$  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.

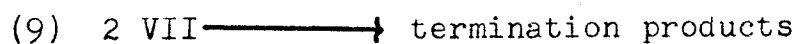
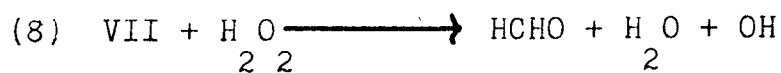
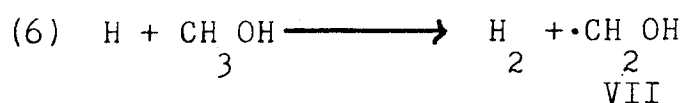
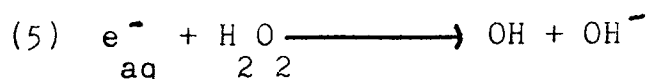
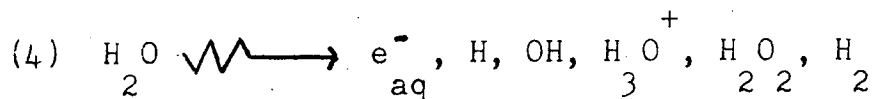


VI

In the presence of  $\text{H}_2\text{O}_2$ , the spectrum of III was also present. At a low  $\text{H}_2\text{O}_2$  concentration, the spectrum of VI disappeared while the concentration of II increased, and the spectrum of III appeared. As the  $\text{H}_2\text{O}_2$  concentration was increased there was a gradual inversion of the concentration.

of II and III. They also reported that the gamma-irradiation of a deaerated aqueous solution of THF and  $\text{H}_2\text{O}_2$  gave a value of 29 for  $G(-\text{H}_2\text{O}_2)$  suggesting the occurrence of a chain reaction.

An investigation of the gamma-radiation induced oxidation of methanol, ethanol, and 2-propanol by  $\text{H}_2\text{O}_2$  in aqueous solutions was reported by Burchill and Ginns (19, 20). The oxidation of methanol was explained by a simple mechanism.

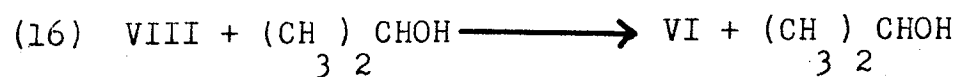
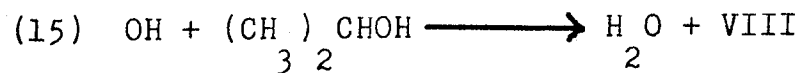
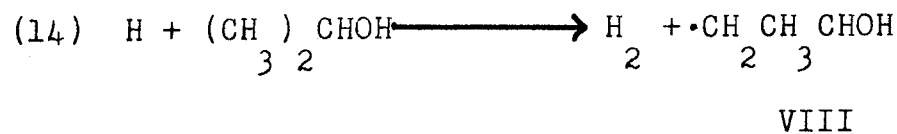
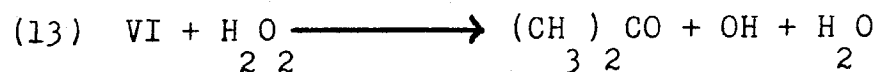
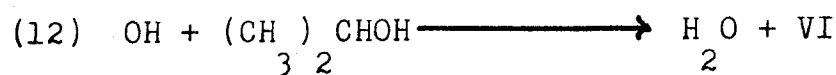
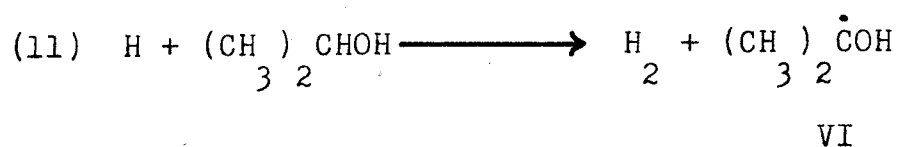
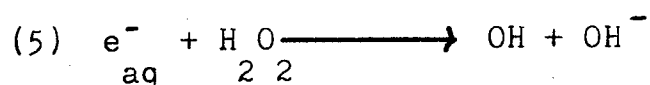
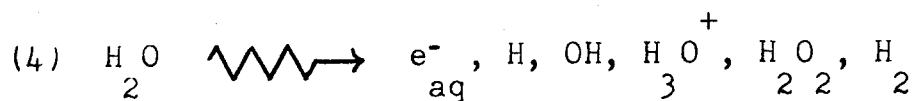


Using the usual steady state assumption, the equation for  $\text{H}_2\text{O}_2$  removal is:

$$(10) \quad \frac{-d[\text{H}_2\text{O}_2]}{dt} = (G_{e_{\text{aq}}^-} - G_{\text{H}_2\text{O}_2}) D + k_8 \frac{[(G_{e_{\text{aq}}^-} + G_{\text{H}} + G_{\text{OH}}) D]^{\frac{1}{2}}}{2k_9} [\text{H}_2\text{O}_2]$$

This equation predicts the rate of  $\text{H}_2\text{O}_2$  removal to be independent of the alcohol concentration, dependent on the square root of the dose rate and first order in  $\text{H}_2\text{O}_2$  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.



(17)  $2 \text{ VIII} \longrightarrow$  termination products

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

$$(18) \quad G(-\text{H O})_{22} = G_{e^- \text{ aq}} - G_{\text{H O}}_{22} + G_{\text{H}} \left\{ \frac{k_{11} (k_{12} + k_{15})}{k_{15} (k_{11} + k_{14})} \right\} +$$

$$\frac{k_{12} (G_{e^- \text{ aq}} + G_{\text{OH}})}{k_{13}} + \left\{ \frac{1 + k_{12}}{k_{13}} \right\} k_{16} \left( \frac{G_{e^- \text{ aq}} + G_{\text{H}} + G_{\text{OH}}}{2k_{17} D} \right)^{\frac{1}{2}}$$

[2-propanol]

The equation predicts a first order dependence on 2-propanol or ethanol concentration, a square root dependence on dose rate, and no dependence on  $\text{H O}_{22}$  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  $\text{H O}_{22}$  oxidation of cyclic ethers is summarized below.

Gamma-irradiation of 1,4-dioxane, in the presence of  $\text{H O}_{22}$ , should give rise to only one radical species, an

$\alpha$ -radical, which is oxidizable by  $\text{H}_2\text{O}_2$  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  $\text{H}_2\text{O}_2$ , should yield two radicals; an  $\alpha$ -radical that can be oxidized by  $\text{H}_2\text{O}_2$  to 2-tetrahydrofuranol and a  $\beta$ -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)



would not be as probable as one like (16). In reaction (19), the abstraction of a H-atom from the methylene group in the  $\alpha$ -position by the  $\beta$ -radical results in the formation of a methylene group in the  $\beta$ -position; while, in reaction (16) the abstraction of the single H-atom in the  $\alpha$ -position by the  $\beta$ -radical yields a terminal methyl group. There should be no effect of  $\text{H}_2\text{O}_2$  concentration. However, deuterium substitution at the  $\beta$ -positions should result in an increased rate of reaction while deuterium substitution at the  $\alpha$ -positions should retard the reaction rate.

1,3-Dioxolane with two radicals of the  $\alpha$ -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 -Tetrahydrofuran (Merck, Sharpe and  
4

Dohme) was used as received.

2,2, 3,3, 5,5, 6,6-d<sub>8</sub>-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 <sup>60</sup>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

<u>Attenuation, %</u>	<u>Dose Rate, eV l<sup>-1</sup> s<sup>-1</sup></u>
100	8.50 x 10 <sup>18</sup>
30	2.33 x 10 <sup>18</sup>
10	7.21 x 10 <sup>17</sup>

### 2.1.3 Dosimetry

The dose rate was measured with the Fricke



dosimeter, an air saturated solution of  $10^{-3}$  M  $\text{FeSO}_4(\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$  in  $0.4\text{M H}_2\text{SO}_4$ . 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  $\text{Fe}^{3+}$  was measured spectrophotometrically at 305 nm using a Carl Zeiss PMQ II spectrophotometer. The molar extinction coefficient was assumed to be  $2.2 \times 10^3 \text{ cm}^{-1}$  and  $G(\text{Fe}^{3+})$  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  $^{60}\text{Co}$ . 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  $\text{H}_2\text{O}_2$ , 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  $H_2O$  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 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 "Vigreux" 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.