RADIATION CHEMISTRY

THE γ-RADIATION INDUCED OXIDATION OF ORGANIC
SOLUTES BY HYDROGEN PEROXIDE IN NEUTRAL
AQUEOUS SOLUTIONS

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by

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ABSTRACT

The radiation induced oxidation of 2-propanol by hydrogen peroxide in neutral deaerated aqueous solution has been investigated. Under these conditions 2-propanol was oxidized to acetone and hydrogen peroxide was removed in stoichiometrically equivalent high yields. The yields were independent of hydrogen peroxide in the range 5×10^{-2} M to 10^{-3} M H_2O_2, and linearly dependent on 2-propanol concentration in the range 0.13 to 1.05 M 2-propanol. The peroxide destruction and acetone formation yields showed an unusual dose rate effect.
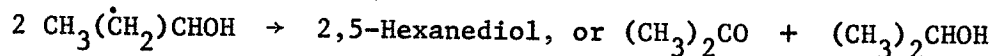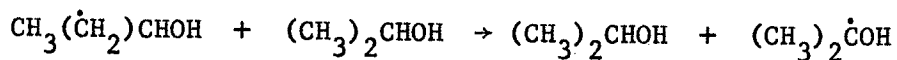
A mechanism was proposed to explain these results. Initially, OH radicals can abstract α- or β-hydrogens from 2-propanol to form $(CH_3)_2\dot{C}OH$ and $CH_3(\dot{C}H_2)CHOH$ respectively. Acetone was formed by the subsequent stoichiometric reaction of H_2O_2 with $(CH_3)_2\dot{C}OH$.

$$(CH_3)_2\dot{C}OH + H_2O_2 \rightarrow (CH_3)_2CO + OH + H_2O$$
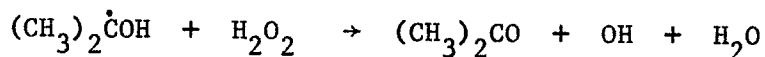
The radical, $CH_3(\dot{C}H_2)CHOH$, may abstract an α-hydrogen from the parent alcohol or undergo a bimolecular termination reaction.

$$CH_3(\dot{C}H_2)CHOH + (CH_3)_2CHOH \rightarrow (CH_3)_2CHOH + (CH_3)_2\dot{C}OH$$

$$2\ CH_3(\dot{C}H_2)CHOH \rightarrow 2,5\text{-Hexanediol, or } (CH_3)_2CO + (CH_3)_2CHOH$$

The radiation induced oxidation of ethanol and methanol was studied to test the generality of the above mechanism. Ethanol and methanol were oxidized to the respective aldehyde and hydrogen peroxide was removed in stoichiometrically equivalent chain yields in each case. The results from ethanol, which can form two distinct radicals ($\cdot CH_2CH_2OH$ and $CH_3\dot{C}HOH$), were similar to those from 2-propanol indicating that the mechanism used to explain the oxidation of 2-propanol can be extended to ethanol.

In the case of methanol, which can form one radical species

only ($\cdot CH_2OH$), the rate of peroxide removal was independent of methanol concentration and shows a first order dependence on peroxide concentration and a square root dependence on dose rate. The contrast with the results from ethanol and 2-propanol was clearly evident.

The presence of thiols (1-propanethiol, 2-propanethiol) as additives has been found to inhibit the γ-radiation induced chain oxidation of 2-propanol by H_2O_2. It was suggested that the presence of thiols protects the 2-propanol substrate from radiation damage by hydrogen transfer from the unionized sulphydryl group in a reaction of the type,

$$(CH_3)_2\dot{C}OH \ + \ RSH \ \rightarrow \ (CH_3)_2CHOH \ + \ RS\cdot$$
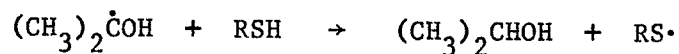
Evidence for this reaction was summarized and a mechanism proposed to account for the inhibition of the chain reaction.

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1. INTRODUCTION

Radiation chemistry is the study of the chemical effects produced in a system by the absorption of ionizing radiation. Types of ionizing radiation include electromagnetic radiation (γ-rays, X-rays) and radiation of a corpuscular nature, (α-particles, β-particles, protons and fission fragments).

1.1 Interaction of Ionizing Radiation with Matter

A knowledge of the processes by which radiation interacts with matter is essential, since the chemical effects produced in a system are a direct result of the absorption of energy from the radiation. Because this work involves the use of Co^{60} gamma radiation exclusively, only the interaction of electromagnetic radiation with matter will be considered.

The physics of the interaction of γ-radiation with matter has been fully discussed elsewhere (1,2,3). Briefly, photons of electromagnetic radiation tend to lose a relatively large amount of energy whenever they interact with matter. The loss of energy can occur by three processes:

(i) Photoelectric Absorption. This process is important for radiation of low energy and material of high atomic number. A photon of radiation is absorbed by an atom with the ejection of a fast electron, usually from one of the inner shells. The electron bears all the energy of the incident photon minus the binding energy of the ejected electron.

(ii) Compton Scattering. In Compton scattering the photons lose part of their energy by ejecting electrons from atoms. Compton scattering is the principal process occurring when Co^{60} gamma rays, with an average energy of 1.25 MeV, interact with water or

other substances of low atomic number.

(iii) Pair Production. The γ-ray photon produces a positron-electron pair within the medium by this process. Pair production cannot occur at photon energies < 1.02 MeV and is significant for photon energies > 10 MeV. Pair production is therefore unimportant in Co^{60} γ-radiolysis experiments.

Gamma rays, whether by photoelectric absorption, Compton scattering or pair production, give rise to fast electrons within the irradiated medium. These electrons have considerable energy ranging up to almost the entire energy of the original photon. The energy required to produce chemical change is only a few eV per molecule, hence a fast electron is capable of altering several thousand molecules. The chief process by which fast electrons cause chemical change is by interaction with the outer electrons of atoms in the absorber. The outer electrons are either excited to higher energy levels or ejected from their atoms or molecules to leave positive ions. This interaction of fast electrons is non-specific.

Ejected (secondary) electrons with high energies can further interact with atoms as described above. Other secondary electrons with low energy but still in excess of ~100 eV form a branch or "delta" ray on the primary track as they lose their energy by ionization. It has been calculated (2) that about one half of the total number of ionizations produced by a primary particle are to be found in the tracks of δ-rays.

Secondary electrons with energies < 100 eV have a short range in liquid or solid materials and any secondary ionizations that they produce will be situated close to the original ionization giving a small cluster or "spur" of excited and ionized species. The greater part of the total ionization in matter is caused by slow electrons either in spurs or along δ-ray tracks. Eventually, the energy of the slow electrons is less than the lowest ionization potential of the medium and

excitation alone occurs as the electrons are captured by molecules or positive ions.

The nature of the ionized or excited intermediates and their consequent reactions depends on the character of the absorber. The specific case of aqueous solutions where water is the main absorber is now discussed.

1.2 γ-Radiolysis of Water and Aqueous Solutions

Co^{60} γ-rays interact with water and aqueous solutions principally by Compton scattering. The fast electrons so formed pass through the liquid losing energy to the molecules either by excitation or by ejecting secondary electrons. Since this process is non-specific, the primary species formed are mainly those derived from water since it forms the bulk of the medium.

The less energetic secondary electrons produce localized concentrations of radicals and ions in the medium. Mozumder and Magee (4,5) have described this process of spur or cluster formation. Initially within the spur will be present ionized water molecules (H_2O^+), electrons (e^-) with an average energy of about 40 eV and excited water molecules (H_2O^*).

$$\{1\} \qquad H_2O \xrightarrow{\sim\!\sim\!\sim} H_2O^+, \ e^-, \ H_2O^*$$
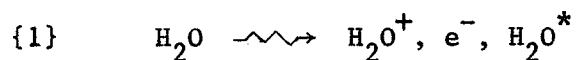
The H_2O^+ ions can react very rapidly with water molecules.

$$\{2\} \qquad H_2O^+ \ + \ H_2O \rightarrow H_3O^+ \ + \ OH$$
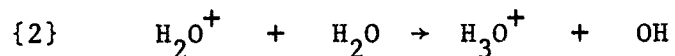
The electrons (e^-) are quickly moderated to subexcitation electrons by collision with water molecules, and then more slowly, in about 5×10^{-13} seconds, reduced to thermal energies (6). The medium may be polarized by orientation of water molecules around the thermal electrons to form hydrated electrons.

$$\{3\} \qquad e^-_{thermal} \ + \ nH_2O \rightarrow e^-_{aq}$$
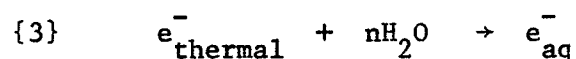
The excited water molecules may dissociate or be deactivated.

$$\{4\} \quad H_2O^* \rightarrow H + OH$$

$$\{5\} \quad H_2O^* \xrightarrow{M} H_2O$$
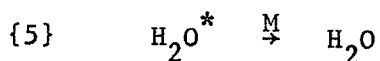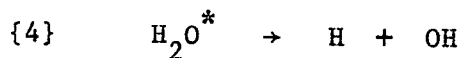
More highly excited water molecules might ionize to e^-_{aq} and $H_2O^+_{aq}$ (7).

Therefore, it is assumed that in about 10^{-11} seconds, the ionized and energy-rich molecules have produced e^-_{aq}, H, OH and $H_3O^+_{aq}$ in relatively high concentrations (6), within spurs that are approximately 5000 Å apart (8).

The identifiable molecular products H_2O_2 and H_2 are assumed to result from the following spur reactions (7,9,10).

$$\{6\} \quad e^-_{aq} + e^-_{aq} \rightarrow H_2 + 2\ OH^-$$

$$\{7\} \quad e^-_{aq} + OH \rightarrow OH^-_{aq}$$

$$\{8\} \quad e^-_{aq} + H_3O^+ \rightarrow H + H_2O$$

$$\{9\} \quad e^-_{aq} + H \rightarrow H_2 + OH^-_{aq}$$

$$\{10\} \quad H + H \rightarrow H_2$$

$$\{11\} \quad H + OH \rightarrow H_2O$$

$$\{12\} \quad OH + OH \rightarrow H_2O_2$$
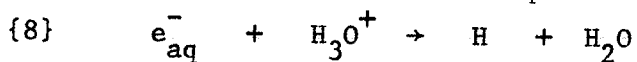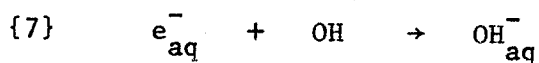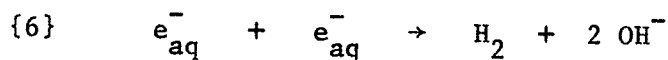
The principal precursor of H_2 is e^-_{aq}, with small amounts contributed by reactions involving H atoms (10). Alternatively, Sworski (11,12) has suggested that H_3O, which results from the capture of e^-_{aq} by $H_3O^+_{aq}$, and H_2O^* are the precursors of H_2.

Process {13} represents the products existing at the end of spur reactions, or at about 10^{-8} seconds after the deposition of energy.

$$\{13\} \quad H_2O \rightsquigarrow H_2,\ H_2O_2,\ H,\ OH,\ e^-_{aq},\ H_3O^+_{aq},\ OH^-_{aq}$$
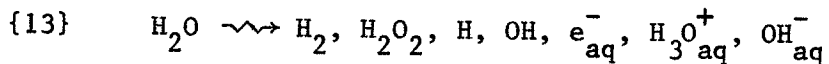
For the purposes of this work, the radiation chemistry of neutral water is presently interpreted in terms of the above process.

The yield, or G-value, of any of these primary species is defined as the number of molecules of the species formed per

100 eV of energy deposited in the system. Since a material balance must be maintained, equation {14} follows.

$$\{14\} \qquad G_{-H_2O} = G_{e_{aq}^-} + G_H + 2G_{H_2} = G_{OH} + 2G_{H_2O_2}$$
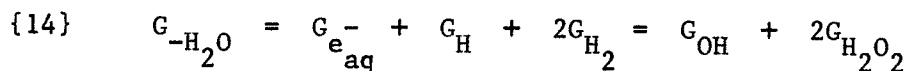
G_X denotes the primary yield of reactive intermediate whilst G(X) denotes the measured yield of a permanent product.

Measurement of primary yields of reactive intermediates has been the subject of intense investigation over the past decade. Much of the work in this area has been reviewed by Buxton (13). All primary yields quoted in this work have been extracted from Buxton's review.

If various solutes are added to water, the reactive intermediates formed in the spur may preferentially attack the solute molecules as the spur expands. In fact the experimental yields of molecular products (H_2 and H_2O_2) and radical products are those measured in the presence of about millimolar concentrations of suitable reactive radical scavengers. The experimental yields do not vary much in the range of reactive scavenger concentrations 10^{-6} to 10^{-3} M. However, at higher solute concentrations primary yields can vary with the concentration of solute present (13). Primary yields can also vary with the pH of the solution (13).

Typical reactions of the intermediate radical species with added solutes will now be discussed. Hydrogen atoms can react either as oxidizing agents or reducing agents. In hydrogen atom abstraction reactions H behaves as an oxidizing agent.

$$\{15\} \qquad H + RH \rightarrow H_2 + R\cdot$$

In donating an electron, or adding to a double bond in an unsaturated compound, H acts as a reducing agent.

$$\{16\} \qquad H + M^{3+} \rightarrow H^+ + M^{2+}$$

$$\{17\} \qquad H + R_2C=CR_2 \rightarrow R_2CH-\overset{\cdot}{C}R_2$$
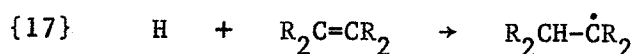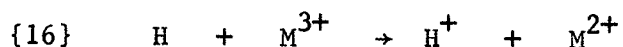
The hydroxyl radical acts exclusively as an oxidizing agent in:

electron transfer reactions,

{18}   OH   + M^{2+} → OH^- + M^{3+}
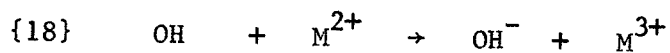
hydrogen atom abstraction reactions from organic solutes,

{19}   OH   +   RH   → H_2O +   R·
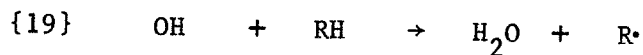
addition reactions to unsaturated substrates.

{20}   OH   + $R_2C=CR_2$ → $HOR_2C-\overset{\bullet}{C}R_2$
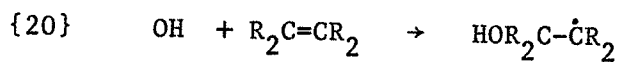
Hydrated electrons in general react as reducing agents in electron transfer processes.

{21} e_{aq}^- + M^{2+} → M^+
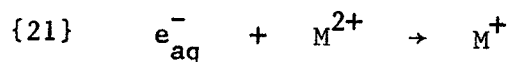
Electron attachment can occur if the solute has vacant orbitals of low energy capable of accepting the electron without unreasonable excitation, for example, systems containing π bonding such as olefins and carbonyl compounds.

{22} e_{aq}^- +   RC=O   → $[RC=O]^-$
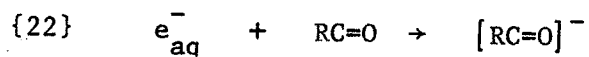
Saturated compounds such as water with no vacant orbitals react extremely slowly if at all.

The rate constants for the reaction of H, OH, e_{aq}^- with a wide variety of solutes, both organic and inorganic, have been determined. Rate constants have been determined indirectly using competition techniques and in many cases absolute reaction rates have been established using techniques such as pulse radiolysis and flash photolysis. An extensive compilation of rate constants for reactions of H, OH, e_{aq}^- has been published by Anbar and Neta (14).

1.3 Scope of Radiation Chemistry

Now that the yields of primary radical species have been well established and many rates of reaction of H, OH, e_{aq}^- have been determined, one must speculate on the future direction

research in radiation chemistry will take.

Pulse radiolysis and flash photolysis have natural extensions into the fields of chemistry and biology. The hydrated electron is only one of several transient species that can be readily studied by either technique. It is possible that much can be and has been learned about the structure of liquids by studying this species. The fields of kinetics and reaction mechanisms are benefitting from the study of all transient species. The presence or absence of spurs in radiation chemistry may be established using advanced techniques in pulse radiolysis. The study of transient species, especially the hydrated electron, is aiding the radiation biologist. The biologist can now use relative reactivities of hydrogen atoms, hydrated electrons and hydroxyl radicals to advantage in explaining biological reactions of dilute model systems where additives such as oxygen and nitric oxide are used. Work is being extended to studies of polymers, proteins, peptides and nucleic acid in concentrated solutions. Results from these systems will be more directly applicable to actual biological systems.

Steady state radiolysis has a wide range of present day applications - for example, food preservation, sterilization of medicinals and pharmaceuticals. Research into these particular fields has taken a rather empirical approach to date. Little research has been undertaken in elucidating the kinds of reactions that occur in the above processes. With the refinement in analytical techniques the radiation chemistry of a wide variety of model biological compounds could be studied by end product analysis. The results could then be extended to the more complex molecules which are present in food and pharmaceuticals. In addition, a knowledge of the radiation chemistry of model biological compounds could be used to explain the reactions occurring in radiation damage to foodstuffs and the reactions of typical biological protective agents such as cysteine and cysteamine.

A potential application of steady state radiolysis is in the preparation of new compounds from simple starting materials. For example, a Co^{60} Gammacell can be used as a source of free radicals for initiating chemical reactions. This could be a valuable tool for preparing fairly complicated molecules from reasonably inexpensive starting materials. However, such reactions, if they were to be ideally suitable for the organic chemist interested in synthetic work or the industrialist interested in commercial applicability, would have to be chain reactions.

With this in mind, it was intended that a study of the radiation induced oxidation of ethylene in the presence of a powerful oxidizing agent should be undertaken. It was hoped that products would be formed in chain yields. The radiolytic oxidation of ethylene in aqueous solution using oxygen as the oxidizing agent had been studied previously (15). Among the products formed were hydrogen, acetylene, carbon monoxide, carbon dioxide, formaldehyde, acetaldehyde and glycolaldehyde. Basson and Du Plessis (15) had noted that a chain mechanism was indicated at low doses.

Initially, a water soluble unsaturated substrate was chosen (allyl alcohol) as a model compound. The radiation induced oxidation of this compound was studied in degassed solutions in the presence of a water soluble oxidizing agent - hydrogen peroxide. The first results indicated that there was no significant chain oxidation of allyl alcohol. Then the study of radiation induced oxidations was extended using 2-propanol as a model compound, and hydrogen peroxide as the oxidizing agent. Preliminary studies indicated that 2-propanol was oxidized to acetone in chain quantities. However, many features of the dependence of the yields on solute concentrations were inconsistent with previous data published in the literature.

Thus an extensive study of the radiation induced oxidation of 2-propanol by hydrogen peroxide was launched. This study was

later extended to the oxidation of other simple alcohols. A survey of the literature pertinent to free radical oxidation of simple organic solutes by hydrogen peroxide now follows.

1.4 Free Radical Induced Oxidation of Simple Organic Solutes -Review

Metal Ion / H_2O_2 Initiation

The mechanism of the oxidation of the alcohols, methanol, ethanol and 2-propanol, by hydrogen peroxide in the presence of an excess of a ferrous salt, has been shown, by quantitive measurements to be as follows (16,17).

Chain initiation,

$$\{23\} \quad Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH + OH^-$$

Chain reaction,

$$\{24\} \quad RCH_2OH + OH \rightarrow R\overset{\bullet}{C}HOH + H_2O$$

$$\{25\} \quad R\overset{\bullet}{C}HOH + H_2O_2 \rightarrow RCHO + OH + H_2O$$
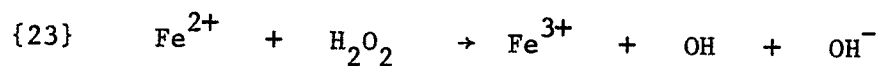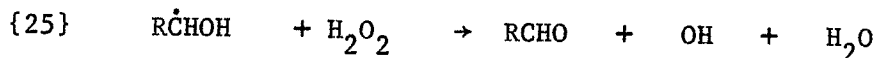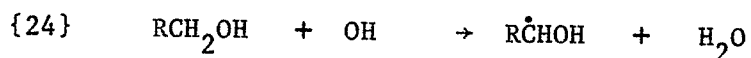
Chain termination at low alcohol concentrations,

$$\{26\} \quad Fe^{2+} + OH \rightarrow Fe^{3+} + OH^-$$
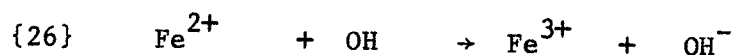
Chain termination at high alcohol concentrations (disproportionation).

$$\{27\} \quad 2 R\overset{\bullet}{C}HOH \rightarrow RCHO + RCH_2OH$$

This mechanism was proposed by Merz and Waters to explain Fenton's reactions (18) whereby polyhydric alcohols, α-hydroxy acids and carbohydrates may be oxidized rapidly by cold hydrogen peroxide in the presence of a ferrous salt.

The reaction of simple organic solutes with the Fenton and Ti(III)/ H_2O_2 systems have recently been studied using fast flow ESR techniques. The interaction of Ti(III) ions and hydrogen peroxide initially gives hydroxyl radicals (19) by an analogous reaction to the Fenton system.

{28} Ti^{3+} + H_2O_2 → Ti^{4+} + OH + OH^-

If the hydroxyl radicals are formed in the presence of a readily
oxidized organic compound, such as methanol, they can be totally
scavenged (20,21), resulting in the formation of $\cdot CH_2OH$ radicals
which can be readily detected by ESR. In studying the Fenton and
$Ti(III)/H_2O_2$ systems by ESR, Norman and West (22) have made
particular use of flow cells which allow one or more reactants
to be added shortly after the others have been mixed, and before
the solution reaches the spectrometer cavity. The results are
consistent with the view that the free hydroxyl radical is the
primary oxidizing agent but that the one-electron oxidation of
the resulting organic radicals by both metal ions and hydrogen
peroxide is important in determining the relative concentrations
of the various radicals which are observed; in this respect
hydrogen peroxide is of special interest because its reduction
by organic radicals leads to the formation of further hydroxyl
radicals and thence the perpetuation of a chain reaction. Neither
the mechanism nor the kinetic implications of the metal ion
catalyzed chain reaction of H_2O_2 with the organic solutes are
discussed by Norman and West.

Thermal Initiation

The thermally initiated reaction of 2-propanol with
hydrogen peroxide in the process of oxidation of 2-propanol to
acetone has been investigated (23,24). Oxygen free nitrogen was
passed through 2-propanol and 30% hydrogen peroxide at 78°C. A
rapid decrease in the concentration of H_2O_2 and 2-propanol was
observed. It was concluded that both the reaction of 2-propanol
with H_2O_2 and the decomposition of H_2O_2 followed a free radical
chain mechanism. The mechanism postulated by Burghardt et al. (24)
is outlined below,

{29} H_2O_2 $\xrightarrow{\text{Thermal}}$ OH + OH

{30}   OH + $(CH_3)_2CHOH$ → H_2O + $(CH_3)_2\dot{C}OH$

{31} $(CH_3)_2\dot{C}OH$ + H_2O_2 → $(CH_3)_2CO$ + OH + H_2O
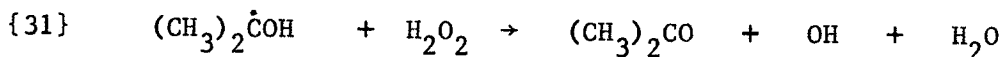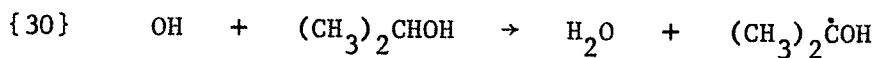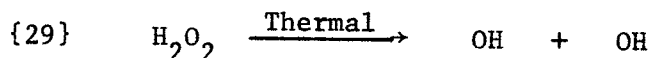
A termination step for the chain mechanism in deoxygenated
solutions was not suggested. In oxygenated solutions reaction
{32} would lead to termination and inhibition of the chain.

{32} $(CH_3)_2\dot{C}OH$ + O_2 → Termination
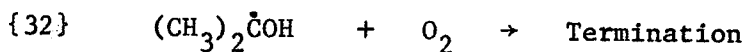
Burghardt also concluded that the reaction of 2-propanol with
H_2O_2 was more important in the absence of oxygen rather than the
presence of oxygen. The more rapid decomposition of H_2O_2 in an
oxygen free atmosphere was explained by an increased reactivity
of $(CH_3)_2\dot{C}OH$ type radicals due to an inductive effect.

Photochemical Initiation

The photolysis of hydrogen peroxide at high light intensities
was studied by Baxendale and Wilson (25). In degassed solutions,
the presence of solutes such as formic acid, ethanol or 2-propanol
induced the chain decomposition of hydrogen peroxide. The
increased quantum yields of peroxide removal were also a function
of the light intensity. With ethanol, acetaldehyde was the major
oxidation product formed by the sequence of reactions,

{33} H_2O_2 $\xrightarrow{h\nu}$ OH + OH

{34}   OH + CH_3CH_2OH → H_2O + $CH_3\dot{C}HOH$

{35} $CH_3\dot{C}HOH$ + H_2O_2 → CH_3CHO + OH + H_2O
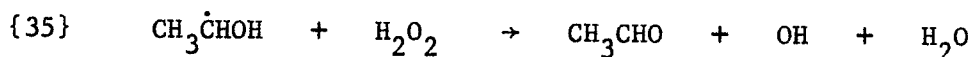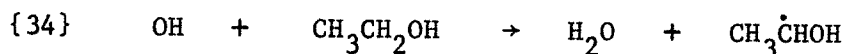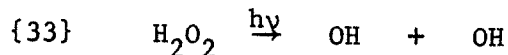
Baxendale does not suggest any possible termination step for this
reaction scheme. However, he does conclude that the analogous
chain reaction with formic acid is terminated by reaction {36}.

{36}   OH + $\cdot CO_2H$ → CO_2 + H_2O
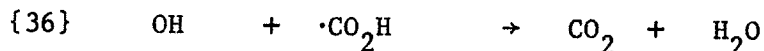
No attempt was made to determine quantitatively the products from the chain oxidation of formic acid, ethanol and 2-propanol.

Barrett et al. (26) have studied the photolysis of hydrogen peroxide in alcohol-water mixtures. In the presence of methanol, ethanol and 2-propanol a chain reaction was induced. As previously suggested by Baxendale, reaction {33} is the initiation step. The hydroxyl radicals so formed react entirely with the alcohol substrate, for example, ethanol,

$$\{34\} \qquad OH \;+\; CH_3CH_2OH \;\rightarrow\; H_2O \;+\; CH_3\overset{\bullet}{C}HOH$$
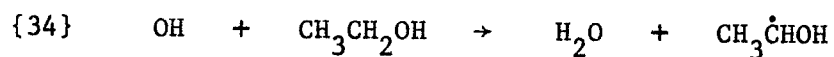
Equation {35} represents the ensuing propagation step with acetaldehyde being the only solution product. The chain yield of peroxide removal reached a maximum value at $\sim$ 2 M alcohol in each case. At higher alcohol concentrations (>2 M) the chain yields gradually decreased to a minimum value in pure alcohol solution. This decrease was attributed to a "cage" effect. Barrett suggests that the respective alcohol radicals may either diffuse from the cage and cause a chain decomposition of the peroxide or they may interact by disproportionation or dimerization within the original solvent cage. As the solute concentration is increased above 2 M, the alcohol radicals tend to interact preferentially within the cage. Fewer radicals will escape the cage to decompose hydrogen peroxide, with a resultant decrease in the quantum yield of peroxide removal.

Radiation Chemical Initiation

Allan and Beck (27) have irradiated aqueous solutions of 10^{-2} M 2-propanol and 10^{-2} M N_2O in order to determine the primary yields of hydrogen atoms and hydrated electrons. They observed that the molecular hydrogen peroxide was present in low stationary-state concentrations in both neutral and acid solutions. The disappearance of H_2O_2 was accounted for by a chain process

initiated by reaction of the organic radical with hydrogen peroxide.

{31} $(CH_3)_2\dot{C}OH$ + H_2O_2 → $(CH_3)_2CO$ + H_2O + OH
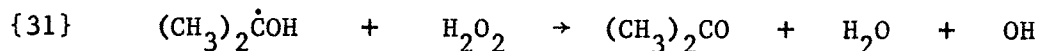
This effect accounted for the high yields of acetone, G(Acetone) ∿ 3, observed in solutions irradiated at low dose rates and for the non-linearity of the acetone yield-dose dependencies. Allan and Beck also suggest that hydroxyl radicals may undergo less specific dehydrogenation reactions with 2-propanol.

{30}   OH + $(CH_3)_2CHOH$ → H_2O + $(CH_3)_2\dot{C}OH$

{37}   OH + $(CH_3)_2CHOH$ → H_2O + $CH_3(\dot{C}H_2)CHOH$
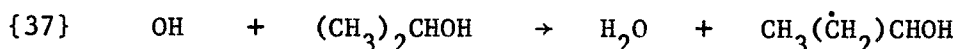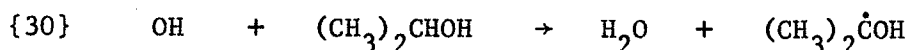
The α-radicals formed by reaction {30} can undergo the propagation reaction {31} or they can disproportionate forming acetone and 2-propanol.

{38}   2 $(CH_3)_2\dot{C}OH$ → $(CH_3)_2CO$ + $(CH_3)_2CHOH$
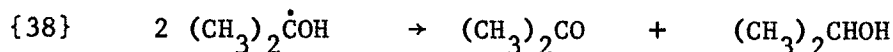
The formation of diol from the combination of α-radicals does not occur (28). Allan and Beck do not discuss the fate of β-radicals formed by reaction {37}.

Seddon and Allen (29) have studied the γ-radiation induced chain reaction of hydrogen peroxide with ethanol in dilute oxygen-free solutions. The peroxide concentration was varied from $(1.22 - 1.97) \times 10^{-4}$ M H_2O_2 whilst the concentration of ethanol was varied from $(1.75 - 10.5) \times 10^{-3}$ M ethanol. A chain process would be expected from the following reactions.

{13} H_2O ⤳ e_{aq}^-, H, OH, H_2O_2, H_2, H_3O^+

{39} e_{aq}^- + H_2O_2 → OH + OH^-

{40}   H + CH_3CH_2OH → H_2 + $CH_3\dot{C}HOH$

{34}   OH + CH_3CH_2OH → H_2O + $CH_3\dot{C}HOH$

{35} $CH_3\dot{C}HOH$ + H_2O_2 → CH_3CHO + H_2O + OH

{41}   2 $CH_3\dot{C}HOH$ → 2,3 Butanediol, or CH_3CHO + CH_3CH_2OH
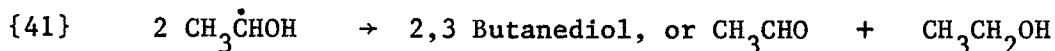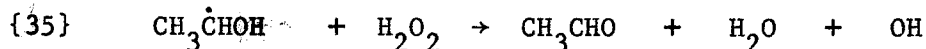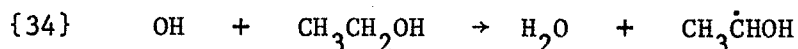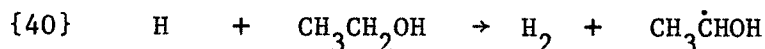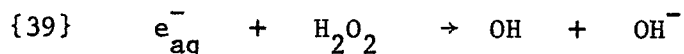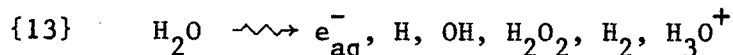
A value of 1.5×10^5 M^{-1} s^{-1} was estimated for k_{35} from pulsed X-ray beam experiments using a Van de Graaff electron accelerator. Seddon and Allen conclude that disproportionation to aldehyde + alcohol occurs in about 30% of the termination reactions {41}. Taub and Dorfman (30) estimate about 20% disproportionation reactions.

Formic acid solutions containing hydrogen peroxide react by a chain mechanism when exposed to ionizing radiations (31,32). Hart explains the chain reaction between formic acid and hydrogen peroxide by reaction {13} followed by reactions {42} and {43} generating ·COOH radicals.

{42} H + $HCOOH$ → H_2 + ·$COOH$

{43} OH + $HCOOH$ → H_2O + ·$COOH$
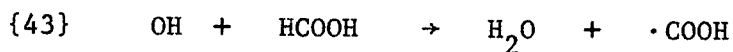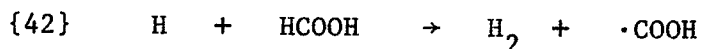
These radicals undergo the propagation reaction,

{44}   ·$COOH$ + H_2O_2 → CO_2 + H_2O + OH
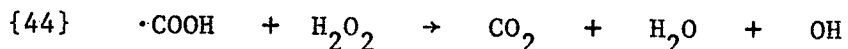
Carbon dioxide is the major product from the chain reaction. Because increased hydrogen peroxide lowered $G(CO_2)$, reaction {45} was suggested as leading to chain termination since the hydroperoxy radical does not propagate the reaction.

{45} OH + H_2O_2 → H_2O + HO_2
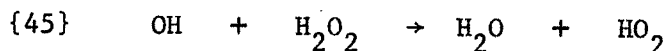
A fuller discussion of the chain oxidation of formic acid by hydrogen peroxide may be found in a review by Hart et al.,(33). Husain and Hart (34) have investigated the above chain reaction over a wide range of pH. To explain the observed effects, the simple chain mechanism is modified to include ionization of carboxyl, hydroperoxy and hydroxyl free radicals, and ionization of formic acid.

Summary

The pertinent features of the radical induced chain

oxidation of simple organic solutes by hydrogen peroxide are
summarized below:

(i) A simple reaction mechanism embodied in the following
general equations has been used to explain experimental results.

{46} $H_2O_2 \xrightarrow{\text{Initiation}} OH + OH$

{24} $OH + RCH_2OH \rightarrow H_2O + R\overset{\cdot}{C}HOH$

{25} $R\overset{\cdot}{C}HOH + H_2O_2 \rightarrow RCHO + OH + H_2O$

{27} $2\ R\overset{\cdot}{C}HOH \rightarrow RCHO + RCH_2OH$
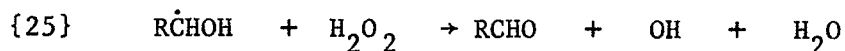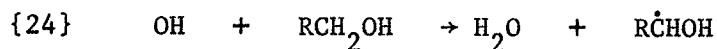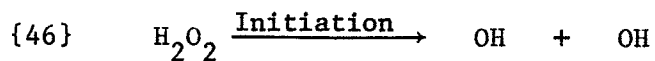
(ii) An expression for the rate of peroxide removal can be
developed using steady state approximations.

{47} $-\dfrac{d\,[H_2O_2]}{dt} = \text{Non Chain Term} + k_{25}\sqrt{\dfrac{\text{Rate of Initiation}}{2\ k_{27}}}\,[H_2O_2]$

(iii) The expression predicts that the rate of peroxide removal
is (a) independent of alcohol concentration,

   (b) dependent on peroxide concentration (first order),

   (c) dependent on the rate of initiation.

As mentioned previously, preliminary studies on the γ-
radiation induced chain oxidation of aqueous 2-propanol by
hydrogen peroxide, indicated that the dependence of yields on
solute concentrations were inconsistent with the features of the
simple mechanism described above. The results of the extensive
study of the 2-propanol /H_2O_2 system are now presented and
discussed in the following sections.

2. EXPERIMENTAL

2.1 Materials

Triply distilled water was prepared by a first distillation of laboratory distilled water from alkaline potassium permanganate and a second distillation from acid potassium dichromate through 60cm reflux columns packed with pyrex tubing. The all pyrex glass distillation set up is described by Hickling (35). Fresh triply distilled water was used in the preparation of stock solutions and for washing all glassware used.

Hydrogen peroxide was supplied in 30% unstabilized aqueous solution (Fisher Certified) and diluted as required.

2-Propanol (Fisher Certified) for the preparation of stock irradiation solutions was used as received.

Ethanol (Canadian Industrial Alcohols and Chemicals Ltd., Absolute) was used without further purification.

Methanol (Fisher Certified) was also used as received.

Tertiary butyl alcohol and allyl alcohol were used as received from the Fisher Scientific Company.

1- and 2-Propanethiol (Eastman) for inhibition studies were used without further purification.

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

2.2 Irradiation Facilities

A Co^{60} Gammacell 220 unit installed by Atomic Energy of Canada Limited was used as the source of γ-radiation for the majority of experiments. The active Co^{60} is contained in pencils arranged vertically around a cylindrical sample chamber, 6 inches

in diameter and 8 inches in height.

The dose a sample receives varies with position. Hence reproducible positioning of samples within the chamber is of prime importance. To facilitate reproducible positioning of samples, cell holders were constructed as described previously (35). The dose rate from the Gammacell could be varied by the use of hollow lead cylinders which fitted into the chamber. The dose rate was nominally attenuated to 30% or 10% of the unattenuated value.

When lower dose rates than could be provided by the Gammacell were required, experiments were undertaken at the Manitoba Cancer Treatment and Research Foundation using an Eldorado Model A Co^{60} Therapy Unit. The dose rate from this source could be varied by placing samples at various distances from the source. The dose rate is uniform over a 20 x 20cm area at 80cm from the source.

Dose rates from the Gammacell and the Eldorado Model A Co^{60} sources for September, 1969 are tabulated below:

TABLE 2.1

Tabulation of Dose Rates

Co^{60} Source	Attenuation	10^{-17} x Dose Rate (eV 1^{-1} s^{-1})
Gammacell 220	Unattenuated	148
	30%	38.4
	10%	13.2
	Distance from Source	
Eldorado Model A	60cm	2.48
	80cm	1.45
	90cm	1.05

2.3 Dosimetry

The dose rates from the Gammacell and Eldorado Co^{60} sources were measured using the Fricke dosimeter, an air saturated solution of 10^{-3} M $FeSO_4(NH_4)_2SO_4 \cdot 6H_2O$ in 0.4 M H_2SO_4. Ten ml of Fricke dosimeter solution was placed in irradiation cells and irradiated for different times. Under irradiation the ferrous ion is oxidized to ferric ion. The concentration of Fe^{3+} produced was measured spectrophotometrically against a blank of unirradiated dosimeter solution at 305 nm using a Carl Zeiss PMQ II spectrophotometer. The extinction coefficient for the measurement of ferric ion at approximately $25^{\circ}C$ in an unthermostated cell holder was taken to be 2.2 x 10^3 M^{-1} cm^{-1}. $G(Fe^{3+})$ was assumed to be 15.6 ions/ 100 eV of dose absorbed (36). Dose rates from the Gammacell were checked regularly. Dose rates from the Eldorado source were measured concurrently with an irradiation run.

The absorption of the Co^{60} γ-radiation by the irradiated solutions is primarily by Compton scattering. Therefore, the actual dose absorbed by a particular solution depends on the electron density of the solution. The dose rate was measured using the Fricke dosimeter and, by comparing the electron densities of the samples with that of the dosimeter solution, an estimate of the true absorbed dose for each sample was made. Sample calculations of true absorbed doses for various solutions have been carried out by Hickling (35).

2.4 Sample Preparation

All glassware used for experimental work was cleaned thoroughly by the following procedure:
The apparatus was washed in either chromic or permanganic acid

and then rinsed with a concentrated nitric acid/ hydrogen peroxide solution. Finally, all glassware was washed several times with each of tap water, distilled water and triply distilled water.

The Pyrex irradiation cells and tap assemblies for attaching the cells to a vacuum line are identical to those described by Hickling (35). After cleaning, the irradiation cells were dried before being filled with sample.

A stock solution was prepared as follows:
An aliquot of 30% unstabilized hydrogen peroxide was transferred to a 100ml volumetric flask. An appropriate volume of organic solute such as 2-propanol was pipetted into the same volumetric flask. Where necessary solutes were weighed directly into the flask. The solution was then made up to volume with triply distilled water.

Ten ml aliquots of a stock solution were pipetted into the irradiation vessels and the vessels were attached by the tap assembly to a vacuum line for degassing. The vacuum line was of all Pyrex glass construction with a mercury diffusion pump. Apiezon N grease was used for all seals. Each sample was degassed by freezing in a solid carbon dioxide/ acetone slurry, pumping and thawing. Four freeze-pump-thaw cycles were sufficient for complete degassing of all samples. The sample bulbs with tap assemblies were then detached and irradiated. Air saturated samples were irradiated directly after preparation. When the Co^{60} Gammacell dose rate was attenuated to 10%, the vessels were sealed off under vacuum and irradiated.

Degassed samples were placed in the appropriate holder and inserted into the Gammacell 220. The samples were not thermostated during the course of the irradiation. Irradiation times were controlled by the automatic timer on the Gammacell. At the Manitoba Cancer Treatment and Research Foundation samples were clamped in place on a stand in front of the Co^{60} source.

The samples were aligned on either side of the horizontal axis of the source. On completion of irradiations the samples were removed and analyzed immediately.

2.5 Analytical Techniques

Spectrophotometry

Wherever possible spectrophotometric techniques of analysis were used. All spectrophotometric measurements were made at room temperature using a Carl Zeiss PMQ II spectrophotometer.

Acetone, the chief product from the oxidation of 2-propanol, was determined by the method of Berntsson (37). To an aliquot of standard acetone or irradiated solution in a 25 ml volumetric flask, the following reagents were added in order: 1ml NaOH (106.25 g/250 ml), 0.25ml salicylaldehyde and 10ml NaOH. The solution was made up to volume with triply distilled water. After two hours of colour development, the solutions were measured against a reference, identical but for the absence of acetone, at 474nm. The solutions remained stable after the initial development period but it was standard practice to take measurements within three hours. A calibration curve for Fisher certified acetone is linear over the concentration region shown in Fig.2.1. The extinction coefficient is found to be 1.79×10^4 $M^{-1} cm^{-1}$. The presence of 2-propanol had negligible effect on the value of the extinction coefficient.

Hydrogen peroxide was measured by the triiodide method (38). Five ml of potassium hydrogen phthalate reagent (12.5g/500 ml) was added to an aliquot of standard peroxide solution or irradiated solution in a 25ml volumetric flask. Secondly, 5ml of iodide reagent (1.25g NaOH; 41.5g KI; 0.125g $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ /500 ml) was added and the solution made up to volume. Colour development is instantaneous and can be measured spectrophotometrically at

<u>Fig.2.1</u>

Beer–Lambert plot for acetone – Salicylaldehyde
method (474 nm).
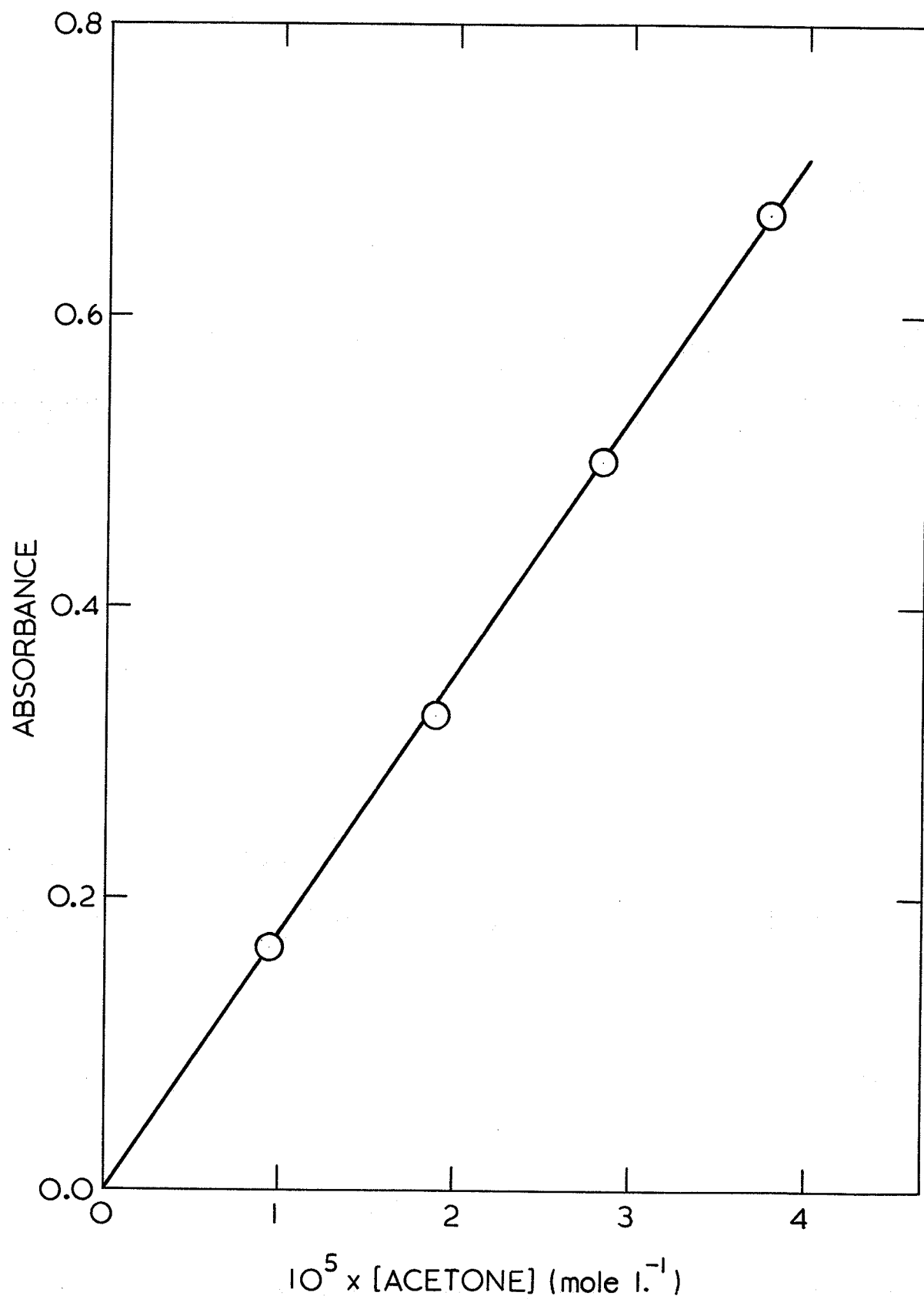
350 nm against a reference identical but for the absence of peroxide. The species measured is the triiodide ion, I_3^-, formed by the reaction,

{48} $H_2O_2 + 3 I^- + 2 H_3O^+ \rightarrow 4 H_2O + I_3^-$
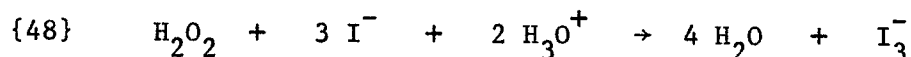
The Beer-Lambert plot for standard peroxide is linear over the concentration range shown in Fig.2.2. The measured extinction coefficient is 2.09×10^4 M^{-1} cm^{-1}. Peroxide solutions were standardized volumetrically against standard ceric sulphate using ferroin indicator.

The triiodide method is unsuitable for determining hydrogen peroxide in the presence of thiols. Therefore, hydrogen peroxide was determined alternately using $Ti(SO_4)_2$ reagent. The $Ti(SO_4)_2$ reagent was prepared by the method described by Snell and Snell (39). Twenty grams of $Ti(SO_4)_2$ was mixed with 20ml concentrated H_2SO_4 and 100ml water. The solution was allowed to stand for 24 hours, then filtered to remove suspended solids. The filtrate was diluted to 240ml and allowed to stand for another two hours. One ml of reagent was then added to an aliquot of standard peroxide solution or irradiated solution and made up to 25ml in a volumetric flask. The colour develops instantly and is stable for six hours. The species measured at 420nm is H_2TiO_4 formed in the reaction,

{49} $Ti^{4+} + H_2O_2 + 2 H_2O \rightarrow H_2TiO_4 + 4 H^+$
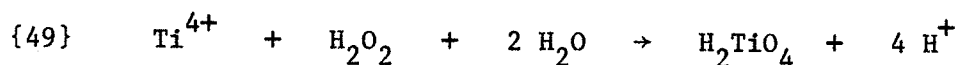
As can be seen in Fig.2.3 the calibration curve for standard hydrogen peroxide is linear with an extinction coefficient of 6.87×10^2 M^{-1} cm^{-1}.

Formaldehyde from the oxidation of methanol was determined by the chromotropic acid (1,8-dihydroxy-naphthalene -3,6-di--sulphonic acid) method (40). Aliquots (0.25 ml) of chromotropic acid solution (2.5g dry acid in 25ml water) were added to various quantities of stock formaldehyde solution in test tubes. Secondly, 2.5ml aliquots of concentrated H_2SO_4 were carefully added to

Fig.2.2

Beer-Lambert plot for hydrogen peroxide -
Triiodide method (350 nm).

$10^5 \times [H_2O_2]$ (mole l.$^{-1}$)
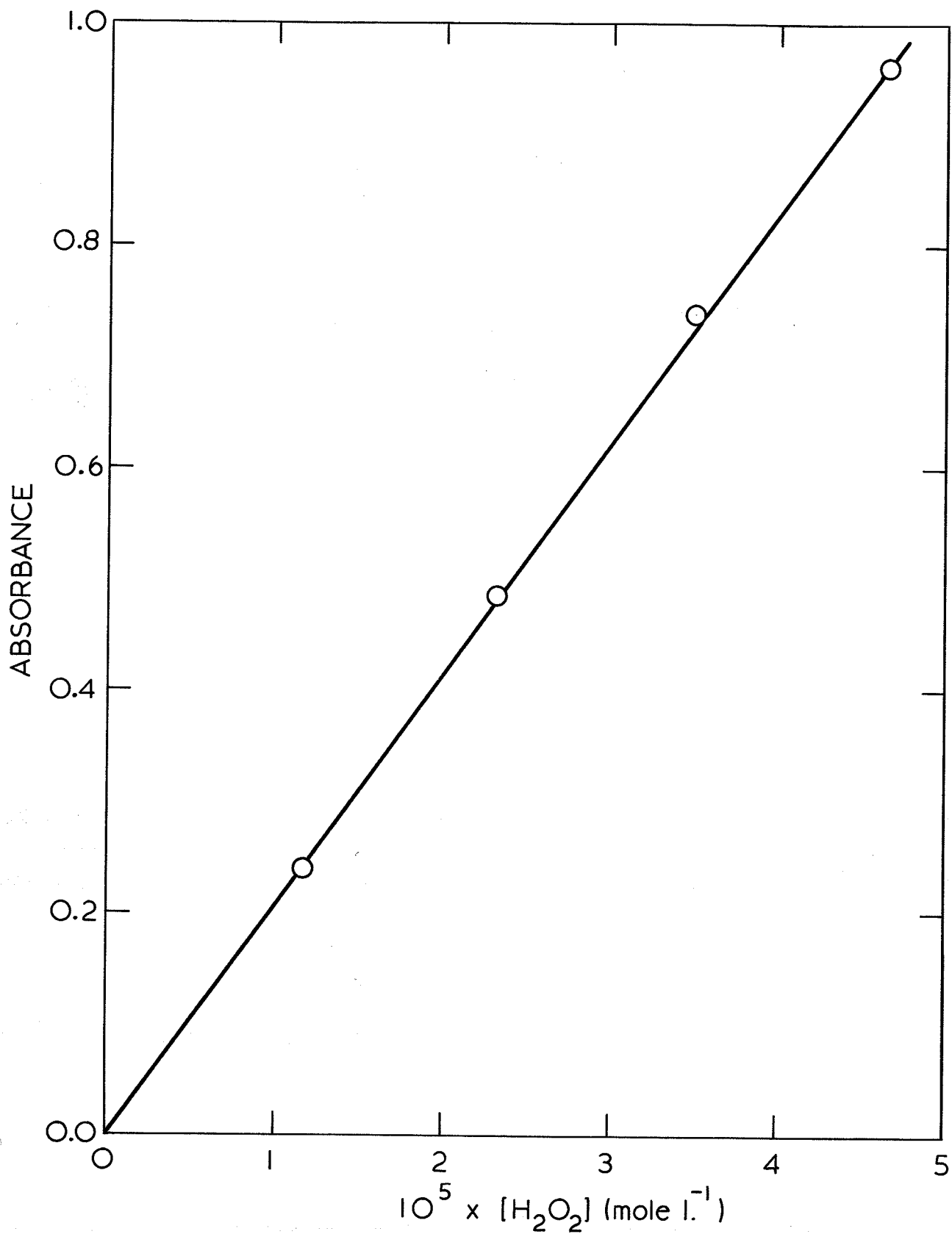
Fig.2.3

Beer-Lambert plot for hydrogen peroxide –
Ti^{4+} method (420 nm).

(24a)

ABSORBANCE vs $10^4 \times [H_2O_2]$ (mole l.$^{-1}$)
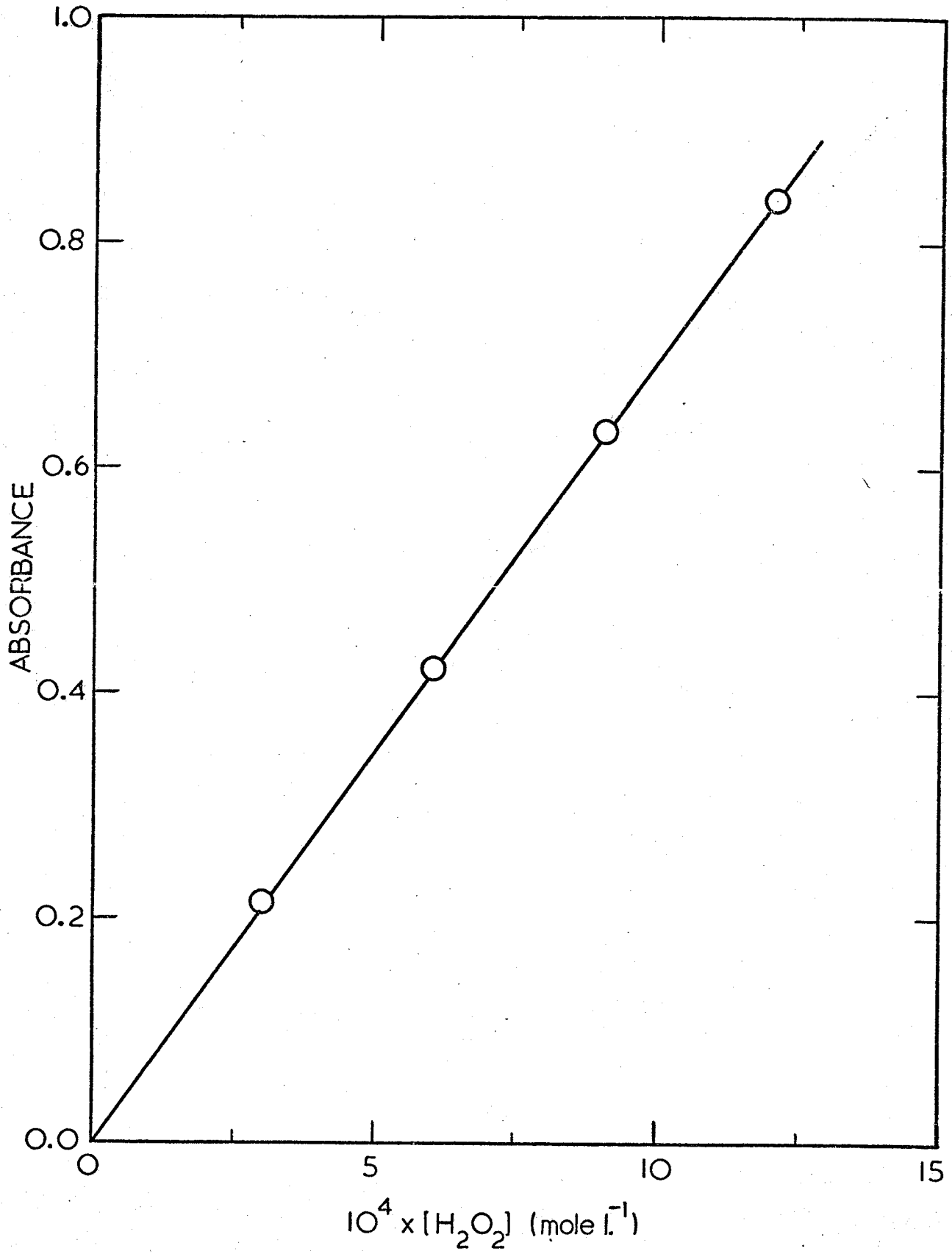
each of the test tubes. The test tubes were then stoppered and placed in a beaker of boiling water for thirty minutes. The tubes were cooled and the contents quantitatively poured into 25ml volumetrics. Finally, the volumes were adjusted to level and the absorbance of each solution measured against a reagent blank at 570nm. The calibration curve for standard formaldehyde (40% w/v HCHO U.S.P.) is linear over the concentration range shown in Fig.2.4. The measured extinction coefficient, $1.54 \times 10^4 \ M^{-1} \ cm^{-1}$, agrees favourably with the literature value $1.57 \times 10^4 \ M^{-1} \ cm^{-1}$ (41).

The chromotropic acid (disodium salt - Technical) was purified before use. Ten grams of the salt were dissolved in 100ml of water. Any insoluble material was filtered off and the filtrate was concentrated to approximately 10ml. The pure crystals were collected, dried and used in the preparation of the chromotropic acid reagent solution.

Gas Chromatography

Acetaldehyde from the oxidation of ethanol was quantitatively determined by gas chromatography using a Victoreen 4001 chromatograph. Acetaldehyde was readily separated from ethanol using a 6 foot column (1/8 inch diameter) packed with Chromosorb 102. Helium was used as the carrier gas (flow rate $\sim$ 30 ml/minute) and detection was by flame ionization. The column temperature was maintained at a constant value of $120^{\circ}C$. Under these conditions acetaldehyde appeared as a uniformly shaped peak whose area could be readily and accurately determined. For quantitative measurements the areas of the acetaldehyde peaks from the irradiated solutions were compared with the peak area from a standard acetaldehyde solution whose concentration was accurately known. Individual concentrations of acetaldehyde could be measured with an accuracy better than $\pm$ 5% by gas chromatography.

Fig.2.4

Beer-Lambert plot for HCHO – Chromotropic
acid method (570 nm).

(26a)
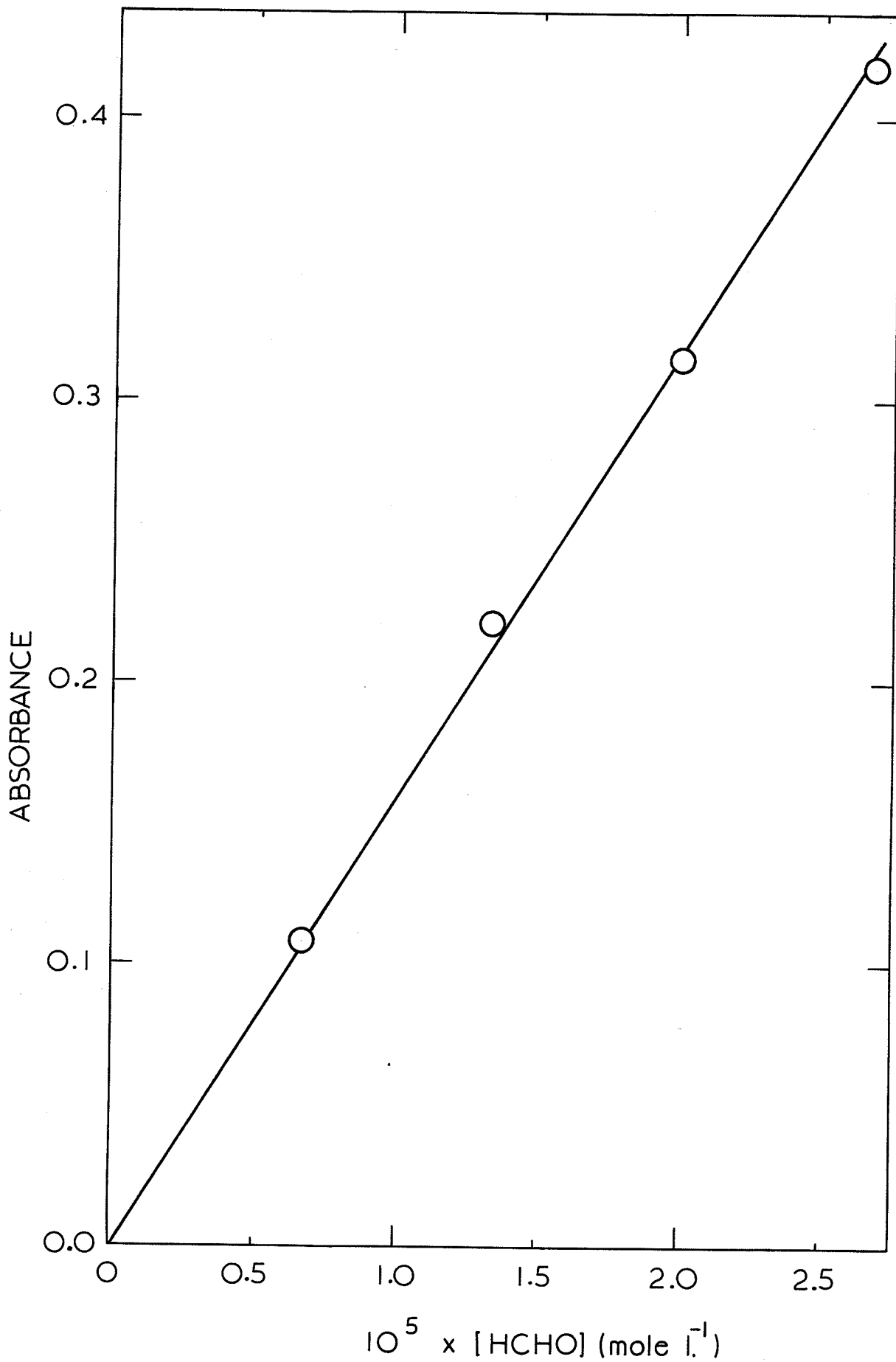
$\underline{2,5\ -Hexanediol}$ was identified as a product in the radiolysis of 2-propanol solutions by gas chromatography. For the identification, a 6ft column packed with 2% Carbowax 20M on 60/80 Chromosorb W was used. The column was maintained at 160°C with Helium as the carrier gas and flame ionization detection. Direct chromatography of the irradiated 2-propanol solutions showed indications of the diol. Each solution was then concentrated by vacuum distillation. When aliquots of the residue were injected into the chromatograph the diol appeared as a sharp peak which compared favourably with peaks obtained from standard solutions of 2,5-hexanediol. Because of the necessity of vacuum distillation, at best semi-quantitative estimates of the amount of diol formed could be made.

$\underline{Ethylene\ glycol}$ was qualitatively detected as a product in the radiolysis of methanol solutions by gas chromatography. A 6ft column of Chromosorb 102 maintained at 200°C was used with Helium as carrier gas and flame ionization detection. Because of the low concentrations involved only rough estimates could be made of the amount of glycol formed during radiolysis.

3. RESULTS AND DISCUSSION - 2-PROPANOL

3.1 Results

A major investigation of the γ-radiation induced oxidation of 2-propanol in deaerated aqueous solutions by hydrogen peroxide has been undertaken. The chain reaction has been studied over a wide range of 2-propanol and hydrogen peroxide concentrations. The results of these investigations are embodied in the following sections.

Degassing was necessary, since initial experiments with aerated solutions indicated that the presence of **oxygen** inhibited the chain reaction.

H_2O_2 Removal Yields

The hydrogen peroxide removal yields in the presence of a constant 2-propanol concentration (0.52 M) are illustrated in a dose-yield plot, Fig.3.1. The figure is a composite graph made up of results taken from runs with several different starting concentrations of hydrogen peroxide. It can be quite clearly seen that the peroxide removal yield is independent of hydrogen peroxide concentration in the range 5×10^{-2} M to 10^{-3} M H_2O_2. Dose-yield plots for peroxide removal are linear and therefore reliable G values for peroxide removal can be calculated from these plots. $G(-H_2O_2) = 51.8 \pm 2.0$ for this particular concentration of 2-propanol. Additional $G(-H_2O_2)$ yields at several different concentrations of 2-propanol are tabulated in Table 3.1.

Acetone Formation Yields

Acetone formation yields for a constant starting concentration

Fig.3.1

Dose-yield plot for H_2O_2 removal.
$[2\text{-Propanol}] = 0.52$ M.
Initial $[H_2O_2]$: (O) 0.05 M
                    (●) 0.03 M
                    (△) 0.02 M
                    (□) 0.01 M
                    (▲) 5×10^{-3} M

(29a)
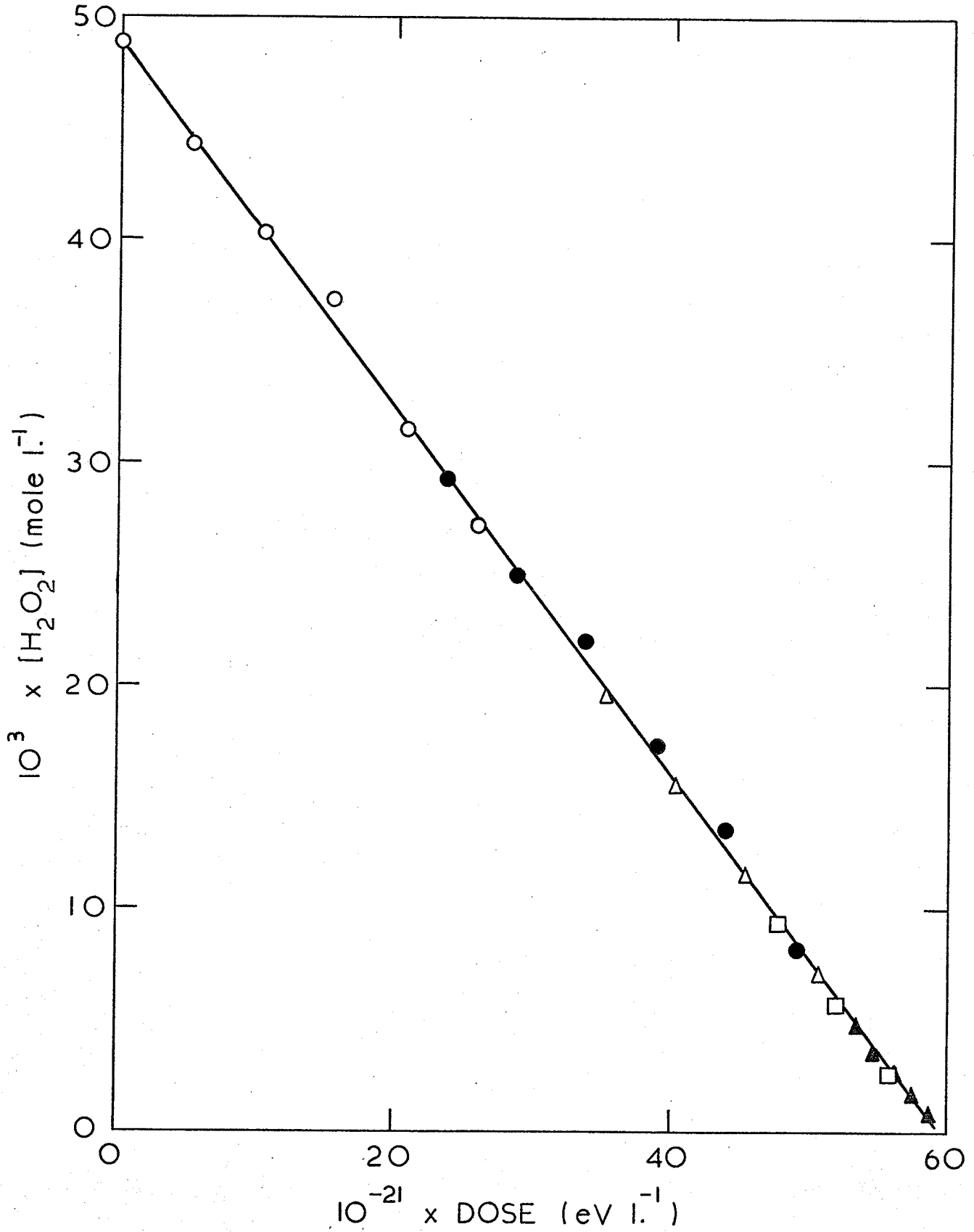
TABLE 3.1

G($-H_2O_2$) and G(Acetone) yields for various
2-propanol concentrations. Initial $[H_2O_2] = 10^{-2}$ M.

[2-Propanol]		G($-H_2O_2$)	G(Acetone)
mole 1^{-1}	mole %		
0.13	0.2	38.1	36.1
0.26	0.5		39.9
0.52	1.0	51.8	51.8
0.78	1.5		58.1
1.05	2.0	70.8	70.1
2.09	4.2		77.4
3.66	8.1		103.3
5.23	13.0		95.7
9.15	33.6		53.1
Pure 2-propanol	100		16.3

of hydrogen peroxide (10^{-2} M) and various concentrations of
2-propanol are shown in Table 3.1. The dose-yield plots for
acetone formation are linear allowing accurate calculation of
G values for acetone formation. A typical dose-yield plot for
acetone formation is shown in Fig.3.2. This Fig.3.2 also clearly
demonstrates the stoichiometric equivalence of acetone formation
and peroxide removal. A similar stoichiometric equivalence of
chain yields was observed on irradiating 2-propanol/H_2O_2 solutions
acidified to pH 1 with perchloric acid.

The peroxide removal yields and acetone formation yields

Fig.3.2

Dose-yield plot for acetone formation and H_2O_2
removal. $[$2-Propanol$]$ = 0.52 M.
Initial $[H_2O_2]$ = 10^{-2} M.

    (O) H_2O_2 removal
    (●) Acetone formation
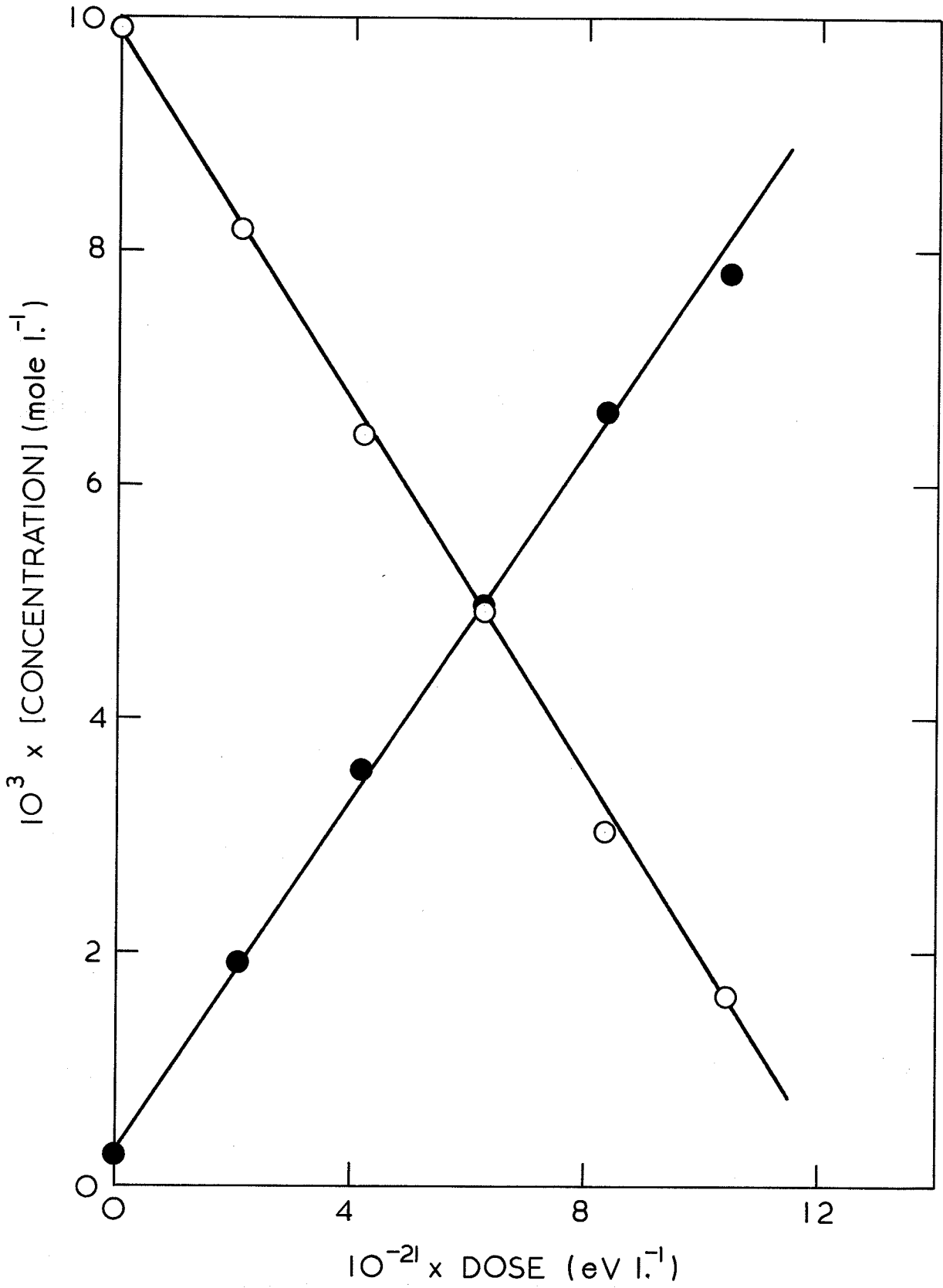
are linearly dependent on the concentration of 2-propanol in the range 0.13 M to 1.05 M 2-propanol. The linear dependence of yields on 2-propanol concentration is shown in Fig.3.3. Extrapolation of both yields as shown in Fig.3.3 leads to the results $G^o(-H_2O_2)$ = 33.4 ± 1.0 and G^o(Acetone) = 31.2 ± 1.0 at zero 2-propanol concentration, indicating a large alcohol independent chain term which must be accounted for by any mechanism proposed. The linear dependence of G(Acetone) on 2-propanol concentration does not hold for concentrations greater than 1.05 M 2-propanol.

The effect of dose rate on the chain formation of acetone for a constant 2-propanol concentration (0.52 M) is illustrated in Fig.3.4. Initial G(Acetone) yields are plotted against $(1/D)^{\frac{1}{2}}$, where D is the dose rate in eV 1^{-1} s^{-1}. The data are also tabulated in Table 3.2. The graph clearly demonstrates that there is a dependence of G(Acetone) on $(1/D)^{\frac{1}{2}}$.

TABLE 3.2

Dose rate effect: G(Acetone) yields at

various values of $(1/D)^{\frac{1}{2}}$. Initial $[H_2O_2]$ = 10^{-2} M.

10^{10} x $(1/D)^{\frac{1}{2}}$ (eV $1^{-1}s^{-1})^{-\frac{1}{2}}$	G(Acetone)
2.39	51.8
5.10	56.5
8.70	70.5
20.07	90.1
26.26	85.9
30.86	$\left\{ \begin{array}{l} 89.6 \\ 79.6^a \end{array} \right.$

a – Initial $[H_2O_2]$ = 3 x 10^{-2} M.

Fig.3.3

G($-H_2O_2$) and G(Acetone) yields as a function of
2-Propanol concentration.

      (O) G($-H_2O_2$)
      (●) G(Acetone)

(33a)
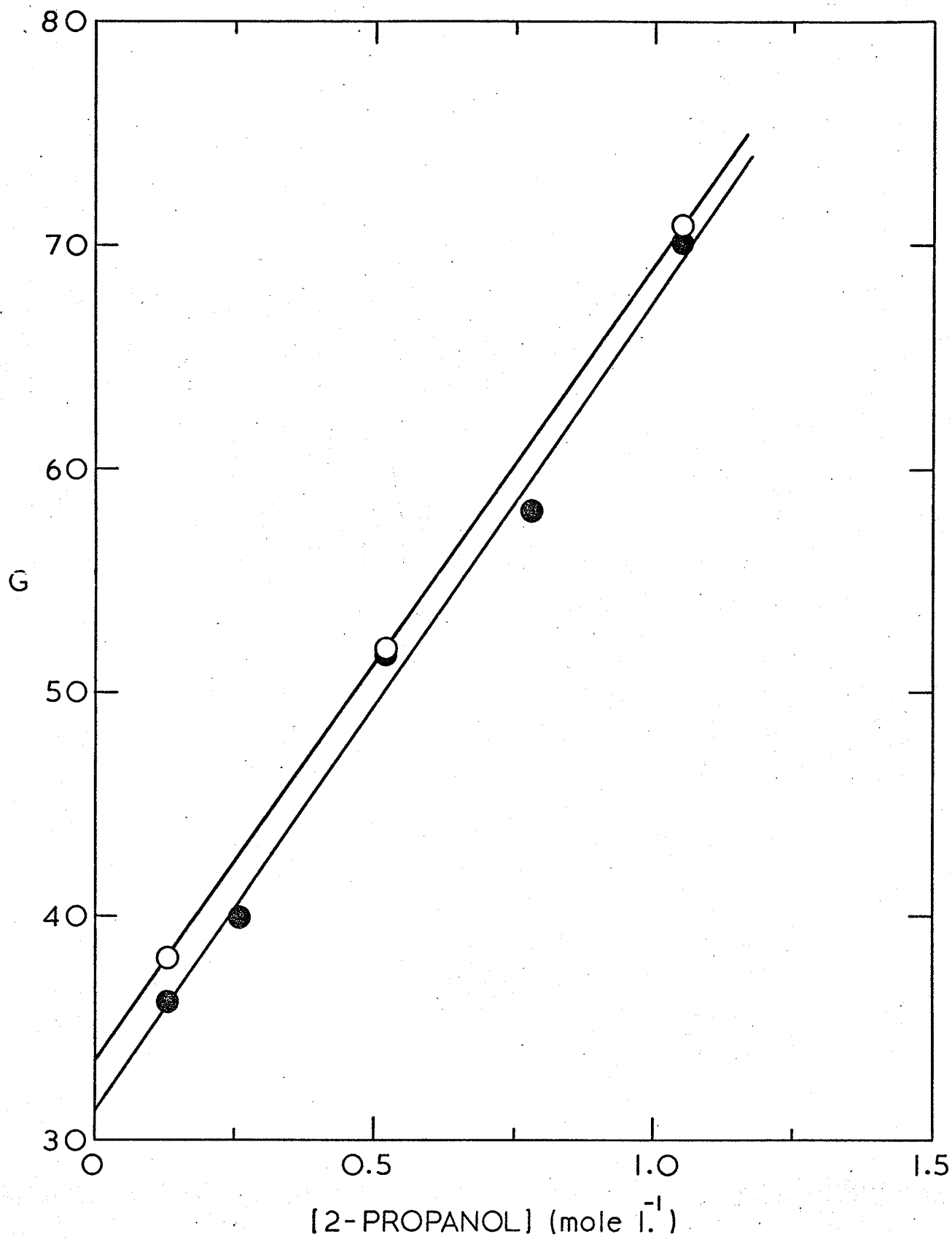
(34)

Fig.3.4

Plot of G(Acetone) against $(1/D)^{\frac{1}{2}}$.
[2-Propanol] = 0.52 M. Initial $[H_2O_2] = 10^{-2}$ M.

(34a)
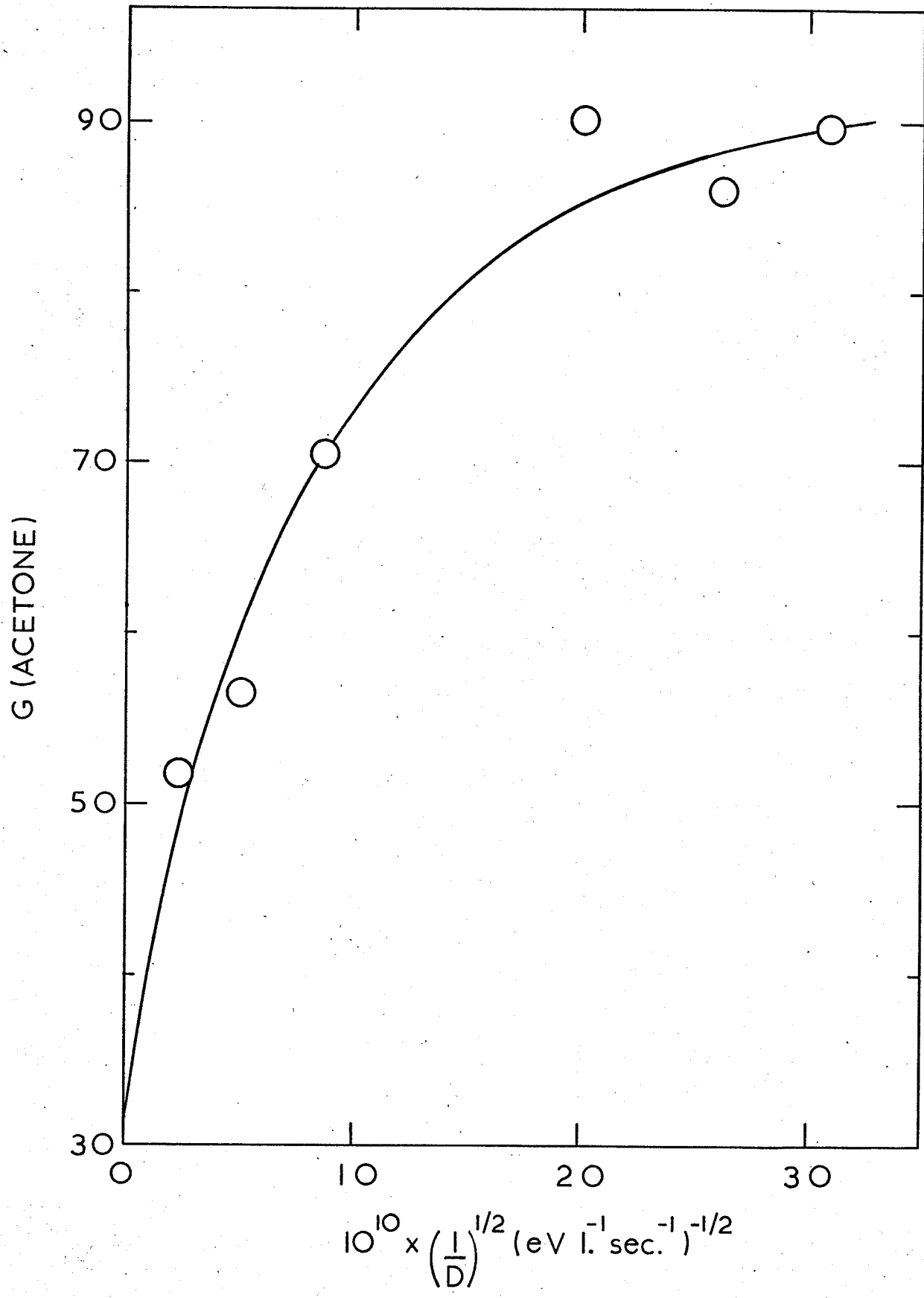
Initial acetone formation yields were obtained for a wide range of 2-propanol concentrations as shown in Fig.3.5. G(Acetone) values are plotted as a function of mole percent 2-propanol. The data are also collected in Table 3.1. From Fig.3.5 it is seen that G(Acetone) increases with increasing mole percent of 2-propanol reaching a maximum value of $\sim$ 100 at a concentration in the vicinity of 3.7 M 2-propanol (8.1%). As the 2-propanol concentration is increased above 3.7 M, G(Acetone) gradually decreases to a limiting value of 16.3 ± 1.0 in straight 2-propanol solution. Table 3.3 contains data demonstrating the effect of altering the dose rate on the yields of acetone formation over a wide range of 2-propanol concentration.

TABLE 3.3

Dose rate effect on G(Acetone).

| [2-Propanol] | G(Acetone) | |
(mole 1^{-1})	Unattenuated	Attenuation to 26%
0.52	51.8	56.5
5.23	95.7	138.3
9.15	53.1	73.7
Pure 2-Propanol	16.3	22.0

H_2O_2 Removal Yields ($<10^{-3}$ M H_2O_2)

Below 10^{-3} M H_2O_2 the peroxide removal yields in the presence of 0.52 M 2-propanol are found to be dependent on peroxide concentration as shown in the dose-yield plot, Fig.3.6. The figure is a composite graph made up of results taken from

Fig.3.5

G(Acetone) plotted as a function of mole
percent 2-propanol.
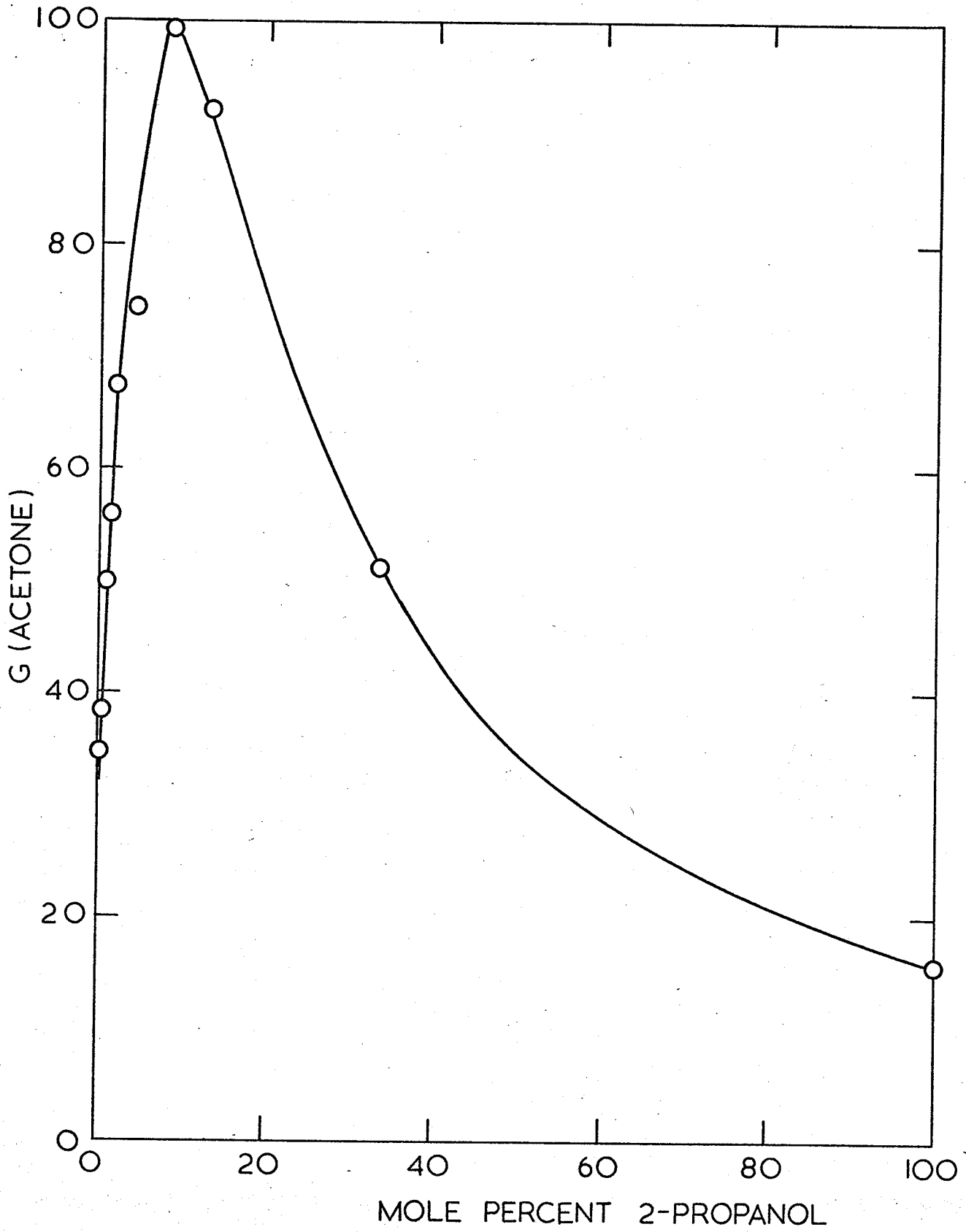
Fig.3.6

Dose-yield plot for H_2O_2 removal for
concentrations of $H_2O_2 < 10^{-3}$ M.
$[\text{2-Propanol}] = 0.52$ M.
Initial $[H_2O_2]$: (O) 5×10^{-3} M
$\qquad\qquad\qquad$ (●) 2.5×10^{-3} M
$\qquad\qquad\qquad$ (△) 10^{-3} M
$\qquad\qquad\qquad$ (■) 3×10^{-4} M

(37a)
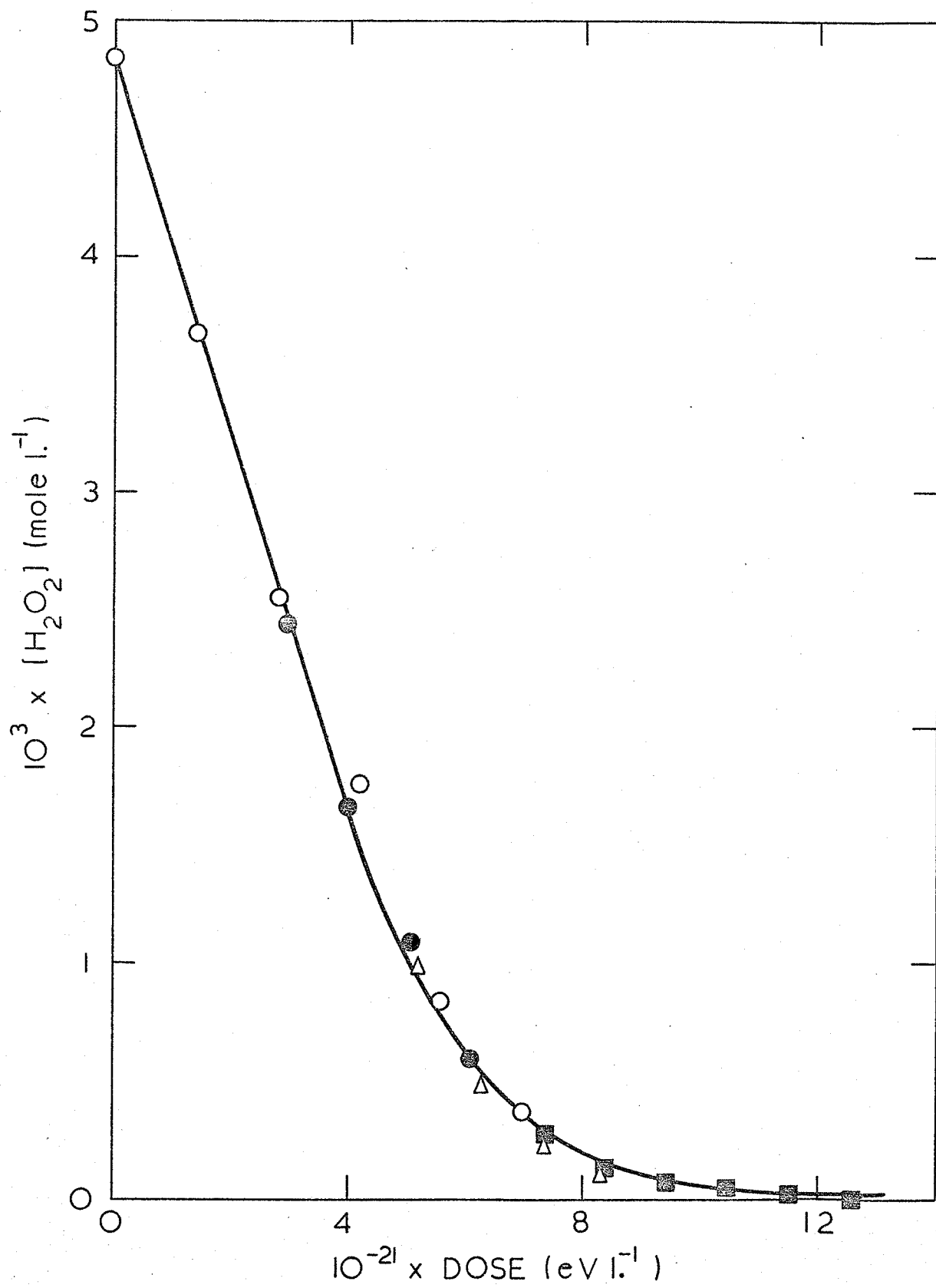
runs using different starting concentrations of hydrogen peroxide. Hydrogen peroxide is removed until a steady-state value of $\sim 3 \times 10^{-6}$ M H_2O_2 is reached. This quantity was found to be rather irreproducible varying by as much as a factor of two from one experiment to another. G(Acetone) at the steady-state concentration of peroxide equals 0.97 ± 0.05.

3.2 Discussion

0.1 - 1.0 M 2-Propanol / $5 \times 10^{-2} - 10^{-3}$ M H_2O_2

In this concentration region the significant features of the results are that the yields of acetone formation and hydrogen peroxide removal are stoichiometrically equivalent, linearly dependent upon the alcohol concentration and independent of the peroxide concentration. The linear plot of G v. 2-propanol concentration extrapolates to a significant chain value at zero alcohol concentration and the radiation-chemical yields show an inverse dependence upon dose rate.

For this range of solute concentrations it may be considered that the γ-radiation specifically interacts with the solvent water.

{13} $H_2O \rightsquigarrow e_{aq}^-$, H, OH, H_3O^+, H_2O_2, H_2
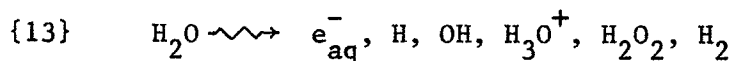
The hydrated electron will react rapidly with the solute hydrogen peroxide.

{39} $e_{aq}^- + H_2O_2 \rightarrow OH + OH^-$
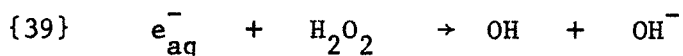
Since $k_{OH + (CH_3)_2CHOH} > k_{OH + H_2O_2}$, $k_{H + (CH_3)_2CHOH} \approx k_{H + H_2O_2}$ (14), and [2-propanol] >> [H_2O_2], all H and OH will react with 2-propanol. Previous authors (16,17,24,25,26) have assumed reaction entirely by abstraction of an H atom from the α-position of the alcohol.

{50}   H   + $(CH_3)_2CHOH$ → H_2 +   I

{30}   OH   + $(CH_3)_2CHOH$ → H_2O +   I
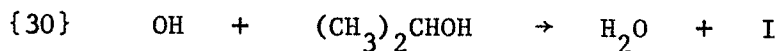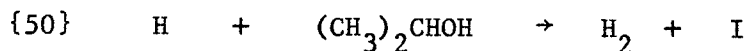
Where I represents the radical $(CH_3)_2\dot{C}OH$. The chain reaction has

been attributed to the propagating reaction {31},

{31}   I   + H_2O_2 → $(CH_3)_2CO$ + H_2O +   OH

with termination of the chain by bimolecular reaction of I.

{38}   2 I   → $(CH_3)_2CO$ + $(CH_3)_2CHOH$
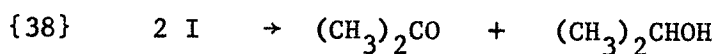
This simple reaction scheme has been shown to predict a
first order dependence of the reaction rate on the concentration
of H_2O_2 and no dependence on alcohol concentration. However, in
these experiments it has been observed that the reaction rate
under irradiation is independent of peroxide concentration and
linearly dependent upon the alcohol concentration.

It is therefore quite clear that the mechanism of the
chain oxidation of 2-propanol by hydrogen peroxide for the range
of concentrations specified is different from the simple scheme
outlined above. A new mechanism must account for the following
points: independence of yields on peroxide concentration; linear
dependence of yields on 2-propanol concentration; a large alcohol
independent chain term as described in the results (Fig.3.3).
The following modifications of the reaction scheme are proposed
to explain the observed results.

The reaction of the hydrated electron will remain unchanged.

{39} e_{aq}^- + H_2O_2 →   OH   + OH^-
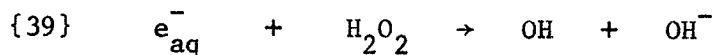
The chain reaction is then initiated by H, OH + 2-propanol
in hydrogen atom abstraction reactions. However, the following
arguments will show that abstraction is not specifically from
the α-position and that abstraction of β-hydrogens from 2-propanol
by H and OH radicals is an important factor in any new mechanism
proposed. The subsequent reactions of the β-radical $CH_3(\dot{C}H_2)CHOH$

derived from 2-propanol have important kinetic consequences.

Anbar and Meyerstein (42) have compared the relative
reactivity of the α- v. β-hydrogens in 2-propanol to hydrogen
abstraction by radiolytically produced hydrogen atoms. Experiments
were carried out in aqueous solutions of 0.04 M 2-d-2-propanol
and acetone. The reactivity of the α-hydrogen toward hydrogen
atom abstraction was found to be 110 times higher than that of
the β-hydrogens. Therefore, although the probability of reaction
{51} is small, it must be considered in addition to reaction {50}.

{51}   H + $(CH_3)_2CHOH$ → H_2 + II
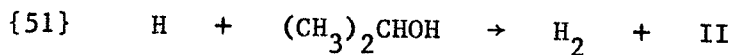
Where II is the radical $CH_3(\dot{C}H_2)CHOH$.

No rate data are available for the abstraction of α- and
β-hydrogens from simple alcohols by OH radicals although it might
be argued that if abstraction by H atoms is not entirely specific
to the α-position, that by OH radicals would be even less specific
by virtue of its greater exothermicity. Allan and Beck (27) suggest
that OH radicals undergo a less specific dehydrogenating reaction
with 2-propanol but do not assess any relative reactivities of
the α- and β-hydrogens. It is suggested that β-hydrogen abstraction
from 2-propanol by OH can occur to a far greater extent than
previously supposed, and must be included in any new reaction
scheme proposed.

{37}   OH + $(CH_3)_2CHOH$ → H_2O + II
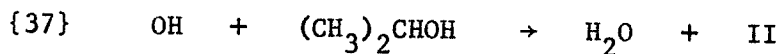
Evidence for the lack of specificity of hydrogen abstraction from
2-propanol by OH is provided from ESR data. Livingston and Zeldes
(43) have observed the ESR spectra of I and II upon photolyzing
a solution of 2-propanol containing 25% water and 1% H_2O_2. The
radicals, I and II, whose formation was attributed to OH radical
abstraction of H atoms from the alcohol, were present in
concentrations within the same order of magnitude. On increasing
the percentage of water the spectrum of radical II became
increasingly prominent. This indicates that to be able to observe

a clear spectrum of the β-radical, β-hydrogen abstraction by OH must readily occur at the solute concentrations Livingston and Zeldes were dealing with. The evidence implies that β-hydrogen abstraction may be of even greater importance in more dilute aqueous solutions of 2-propanol.

The β-radical, $CH_3(\dot{C}H_2)CHOH$, can be regarded as being similar to an alkyl radical. It is known that alkyl radicals such as $\cdot CH_3$ can abstract hydrogen from the α-position of 2-propanol (44) and it is not unreasonable to predict that radical II can undergo a similar reaction.

{52}   II + $(CH_3)_2CHOH$ → $(CH_3)_2\dot{C}HOH$ + I
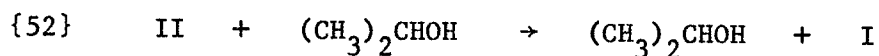
This radical conversion reaction {52} is suggested, in part, by the form of the experimental results. The linear dependence of the radiolytic yields on alcohol concentration suggests that the chain length is determined by the competition between a radical terminating reaction and the reaction of that radical with the alcohol. In view of the high rate of its reaction with the alcohol (14) and the large concentration of the alcohol it is unlikely that the steady-state concentration of OH is sufficient for it to play any role in chain termination. Chain termination involving radical I would be in competition with the propagating reaction {31} and would lead to some dependence of chain length on H_2O_2 concentration which is not observed in the results. There remains the possibility of reaction {52} as the rate controlling propagation step in competition with reaction {53} as the terminating step.

{53}   2 $CH_3(\dot{C}H_2)CHOH$ → 2,5-Hexanediol, or $(CH_3)_2CO$ + $(CH_3)_2CHOH$
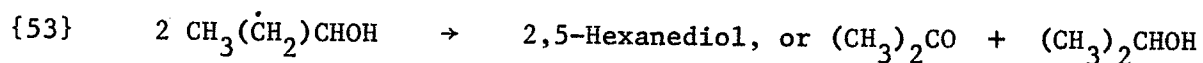
While this competition between reactions {52} and {53} appears to predict the appropriate kinetic form of the results, this is not sufficient to conclude that reaction {52} occurs. Examination of the literature, however, has brought to light considerable

(42)

evidence that such a conversion reaction may occur.

Livingston and Zeldes (45) observed that a strong ESR spectrum of $(CH_3)_2\dot{C}OH$ was obtained from the photolysis of pure 2-propanol containing 1% H_2O_2 but no spectrum of the radical formed by β- abstraction was observed. This evidence supports the suggestion that the conversion reaction {52} can occur. Although reaction {52} may be a slow reaction it is possible that in pure 2-propanol all β-radicals could be converted to $(CH_3)_2\dot{C}OH$ before they are detected in the ESR cavity. Consequently, as the concentration of 2-propanol is lowered, the probability of reaction {52} decreases with an increasing probability of detecting the β-radicals, as has been observed (43). It was also noted that as the solution (75% 2-propanol; 25% H_2O) is cooled from 30° to -5^oC the line intensities due to the β-radical are intensified implying a higher steady-state concentration of II and that fewer β-radicals are undergoing the conversion reaction {52} at the lower temperature. This observation is consistent with the occurrence of reaction {52} , a slow reaction with a significant activation energy.

Norman and West (22) have recently used the conversion reaction {52} to explain results from ESR studies on the reactions of organic compounds with the OH radical derived from hydrogen peroxide and metal ions. At constant concentrations of titanium (III) ion and hydrogen peroxide (0.008 M and 0.05 M respectively), they observed that the ratio of the concentrations of the radicals I and II increased as the 2-propanol concentration was raised. They suggested that the occurrence of reaction {52} could explain these results. Their results certainly agree with the suggestion that the probability of reaction {52} increases with increasing 2-propanol concentration.

The postulates of significant β-hydrogen abstraction by OH radicals and the presence of conversion reaction {52} can be used to account for unusual results in the vapour phase oxidation

of 2-propanol by $O(^3P)$ atoms (46). Kato and Cvetanovic noted a 15% reduction in the yield of acetone on reducing the 2-propanol pressure from 40 to 10 torr. High 2-propanol pressures correspond to concentrated solutions of 2-propanol where the probability of reaction {52} is high, hence $(CH_3)_2\dot{C}OH$ radicals would be the sole remaining radical species produced from 2-propanol. These radicals dimerize to form pinacol or disproportionate to form acetone + 2-propanol in the yields found by Kato and Cvetanovic. Low 2-propanol pressures correspond to dilute solutions of 2-propanol where a significant amount of β-radicals will be present because of the low probability of the conversion reaction {52}. Hence a lower steady-state concentration of α-radicals will be present resulting in a decreased acetone yield at low 2-propanol pressures. The β-radicals would probably undergo a combination reaction to form 2,5-hexanediol. Kato and Cvetanovic make no mention of having looked for such a product nor do they quote any pinacol formation yields at low 2-propanol pressures.

The preceding evidence clearly supports the suggestion that a conversion reaction {52} can and does occur and justifies the inclusion of this reaction in a new mechanistic scheme.

{52}   II   + $(CH_3)_2CHOH$ → $(CH_3)_2CHOH$ +   I
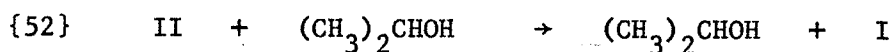
The chief product acetone is formed by the stoichiometric reaction of H_2O_2 with $(CH_3)_2\dot{C}OH$.

{31} $(CH_3)_2\dot{C}OH$ + H_2O_2 → $(CH_3)_2CO$ +   OH   + H_2O
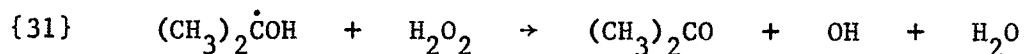
Oxidation of the β-radical, II, by H_2O_2 is excluded. Support for this conclusion comes from the work of Adams and Willson (47) who observe that β-radicals are much less reactive as reductants than α-radicals. From ESR evidence, Norman and West (22) have concluded that the radical $(CH_3)_2\dot{C}OH$ reacts with hydrogen peroxide far more rapidly than does the radical $CH_3(\dot{C}H_2)CHOH$.

The latter radical (oxidation of which gives a primary carbonium ion) should be a less effective one electron donor than the former. In this laboratory it has been shown that the radiation induced oxidation of aqueous solutions of either allyl alcohol or t-butyl alcohol by H_2O_2 is negligible. Allyl alcohol predominantly forms β-radicals by addition of H and OH across the double bond (48). A small yield of $G(-H_2O_2)$ ∿3 is obtained. With t-butyl alcohol, which forms β-radicals only, a small chain peroxide removal yield of $G(-H_2O_2)$ ∿7 is observed.

The termination reaction {38} may be deleted from the proposed mechanism. As discussed before, if such a reaction did occur it would be in competition with the propagation reaction {31} and would lead to some dependence of chain length on H_2O_2 concentration. However, termination of the chain can proceed by the bimolecular combination or disproportionation of two β-radicals to form 2,5-hexanediol, or acetone + 2-propanol respectively.

{53}   2 II   →   2,5-Hexanediol, or $(CH_3)_2CO$ + $(CH_3)_2CHOH$
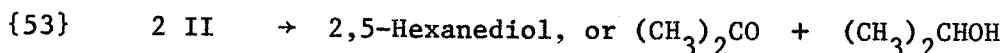
If the product of reaction {53} were entirely diol, a yield of about G(Diol) = 2.5 would be expected. From the results obtained it is concluded that dimerization occurs in at least 15 – 20% of the termination reactions. The remainder of the termination reactions proceed by disproportionation. The termination reaction {53} is in competition with the rate controlling propagation step {52}, accounting for the dependence of yields on 2-propanol concentration.

The new reaction scheme to describe the oxidation of 2-propanol by hydrogen peroxide is summarized below:

{13} H_2O ⤳ e^-_{aq}, H, OH, H_3O^+, H_2O_2, H_2

{39} e^-_{aq} + H_2O_2 → OH + OH^-

{50}   H + $(CH_3)_2CHOH$ → H_2 + I

{30} OH + $(CH_3)_2CHOH$ $\rightarrow$ H_2O + I

{31} I + H_2O_2 $\rightarrow$ $(CH_3)_2CO$ + OH + H_2O

{51} H + $(CH_3)_2CHOH$ $\rightarrow$ H_2 + II

{37} OH + $(CH_3)_2CHOH$ $\rightarrow$ H_2O + II

{52} II + $(CH_3)_2CHOH$ $\rightarrow$ $(CH_3)_2CHOH$ + I

{53} 2 II $\rightarrow$ 2,5-Hexanediol, or $(CH_3)_2CO$ + $(CH_3)_2CHOH$
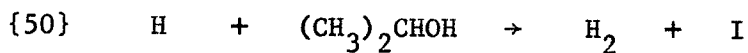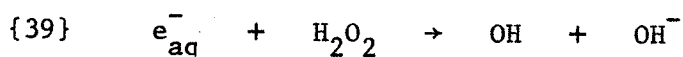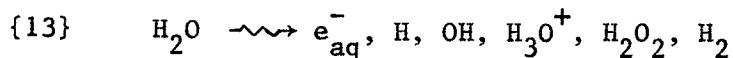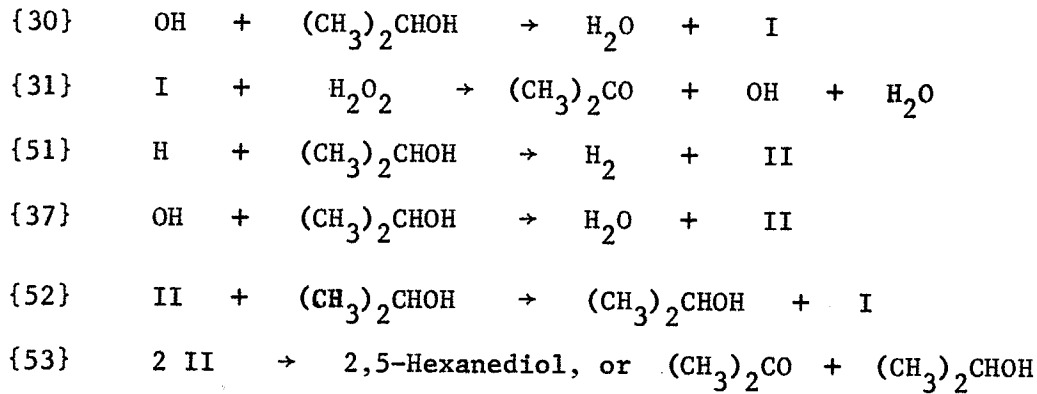
Assuming normal steady-state approximations for the above reaction scheme, an expression may be derived for the radiation chemical yields in the system.

$$\{54\}\quad G(-H_2O_2) = \left[G_{e_{aq}^-} - G_{H_2O_2} + G_H\left\{\frac{k_{50}(k_{30} + k_{37})}{k_{37}(k_{50} + k_{51})}\right\} + \frac{k_{30}(G_{e_{aq}^-} + G_{OH})}{k_{37}} \right]$$

$$+ \left(1 + \frac{k_{30}}{k_{37}}\right)k_{52}\left(\frac{G_{e_{aq}^-} + G_H + G_{OH}}{2 k_{53} D}\right)^{\frac{1}{2}} [(CH_3)_2CHOH]$$

(D is the dose rate in units of 6.02×10^{25} eV 1^{-1} s^{-1})

G(Acetone) differs only marginally from $G(-H_2O_2)$ depending upon the exact stoichiometry of the terminating reaction {53}.

The portion of expression {54} in square brackets predicts a large alcohol independent chain yield which agrees with the results as represented in Fig.3.3. At zero 2-propanol concentration $G^o(-H_2O_2) = 33.4$. Assuming the following values for $G_{e_{aq}^-}$, G_H, G_{OH}, $G_{H_2O_2}$ (13) and the rate constants k_{50}, k_{51} and $k_{30} + k_{37}$

(14), the rate constant ratio k_{30}/k_{37} (or k_α/k_β) can be readily calculated.

$$G_{e^-_{aq}} = 2.28 \qquad k_{50} = 5 \times 10^7 \ M^{-1} \ s^{-1}$$

$$G_H = 0.57 \qquad k_{51} = 2.5 \times 10^6 \ M^{-1} \ s^{-1}$$

$$G_{OH} = 2.25 \qquad k_{30} + k_{37} = 1.4 \times 10^9 \ M^{-1} \ s^{-1}$$

$$G_{H_2O_2} = 0.77$$

The ratio was found to be $k_{30}/k_{37} = 6.2$. The low value for the rate constant ratio confirms the prediction that abstraction of β-hydrogens from 2-propanol by OH is an important factor in the mechanism. Assuming the value of $k_{30} + k_{37}$ to be $1.4 \times 10^9 \ M^{-1} \ s^{-1}$ (14) gives:

$$k_{30} = 1.2 \times 10^9 \ M^{-1} \ s^{-1}$$

$$k_{37} = 2.0 \times 10^8 \ M^{-1} \ s^{-1}$$

In addition the non-specificity of hydrogen abstraction by OH has been suggested by results from pulse radiolysis experiments (47). The oxidation of simple organic radicals was followed by direct measurement of the bleaching of the optical absorption spectrum of the ferricyanide ion. Two component bleaching kinetics indicated that more than one radical oxidation process was occuring. The more rapid component was attributed to the oxidation of the α-radical, for example, for 2-propanol,

{30} $OH + (CH_3)_2CHOH \rightarrow (CH_3)_2\overset{\cdot}{C}OH + H_2O$

{55} $(CH_3)_2\overset{\cdot}{C}OH + [Fe(CN)_6]^{3-} \rightarrow (CH_3)_2CO + H^+ + [Fe(CN)_6]^{4-}$
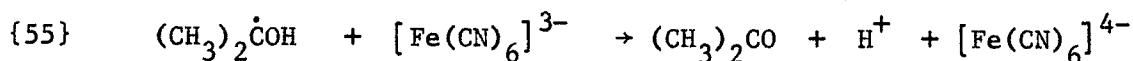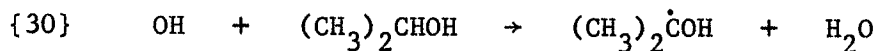
The slower process was attributed to the oxidation of radical products formed by hydrogen abstraction from sites other than the α-carbon atom. Adams states that the decay processes were usually too slow to avoid kinetic complications arising from

competition by radical-radical reactions of the type,

{53}   2 II → 2,5-Hexanediol, or $(CH_3)_2CO$ + $(CH_3)_2CHOH$
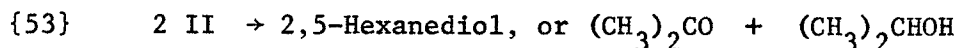
A value of 95% attack by OH at the α-position in 2-propanol was obtained by direct measurement of the fraction of ferricyanide bleached in the rapid process compared with that observed in methanol solution (100% α-carbon attack) irradiated under iso- -dose conditions. Approximately 5% error is involved in making this measurement, hence the value of 95% for percentage α-attack can be regarded as an upper limit. Although this percentage is somewhat higher than the value of 86% α-attack in 2-propanol obtained from k_{30}/k_{37} = 6.2, the evidence further supports the postulate that hydrogen atom abstraction by OH is less specific than previously supposed.

The second portion of expression {54} predicts a linear dependence of the yields on 2-propanol concentration and no dependence on peroxide concentration which conforms precisely to the experimental results as shown in Figs.3.1 and 3.3. The coefficient of [2-propanol] corresponds to the slope of the line in Fig.3.3. However, this coefficient includes a dose rate dependent term which predicts an inverse square root dependence of yields on the dose rate and extrapolation to the zero alcohol intercept at high dose rates. As can be seen from Fig.3.4 G(Acetone) is not the predicted linear function of $(1/D)^{\frac{1}{2}}$, although the yield decreases with increasing dose rate and the curve can, without difficulty, be extrapolated to the appropriate intercept. The fact that there is a dose rate effect confirms that a bimolecular termination process such as {53} is occurring, but the curvature of Fig.3.4 indicates that there is in addition an apparent first order termination which becomes increasingly important at low dose rates.

If it is assumed that at the highest dose rate used $(1.75 \times 10^{19}$ eV 1^{-1} $s^{-1})$ termination is primarily by the bimolecular

process {53} it is possible to estimate a lower limit for the rate constant of the conversion reaction {52}. Using k_{30}/k_{37} = 6.2 and Buxton's values for the primary radical yields (13) and assuming a value of 2 k_{53} = 2.0 x 10^9 M^{-1} s^{-1} for the bimolecular termination reaction, the rate constant k_{52} can be calculated from the slope of G($-H_2O_2$) v. [2-Propanol] (Fig.3.3). The lower limit of k_{52} so estimated is 53 ± 15 M^{-1} s^{-1}. This estimate is nearly two orders of magnitude less than the observed rate constant for the corresponding methyl radical reaction {56},

{56} $\cdot CH_3$ + $(CH_3)_2CHOH$ → CH_4 + $(CH_3)_2\dot{C}OH$
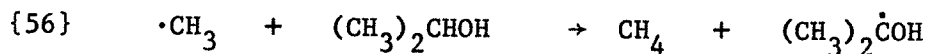
but this, in view of the highly ordered transition state required for such a reaction, may not be unreasonable.

Thomas (44) has noted that the absolute value of $\cdot CH_3$ radical rates is significantly less than the corresponding H atom rates and that this is due to two factors: a) the methyl radical is planar and an activation energy is required to reach the transition state which has the character of the tetrahedral methane molecule, and b) the pre-exponential or A factors for methyl radical reactions are much smaller than the A factors for H atom reactions due to the significant amount of entropy lost by the $\cdot CH_3$ and the solute in forming the transition state of the reaction. Reaction {52} would have a similar activation energy to reaction {56} , however, the transition state for reaction {52} would be more ordered than the analogous methyl radical reaction resulting in an even smaller A factor than for the $\cdot CH_3$ reaction {56}. Therefore, k_{52} should be less than k_{56} (k_{56} = 3.4 x 10^3 M^{-1} s^{-1} – 44) which is in fact observed.

As previously noted in the results, the presence of acid has no effect on G(Acetone) and G($-H_2O_2$) yields. In acid solution the hydrated electron would preferentially react with the acid.

{8} e_{aq}^- + H_3O^+ → H + H_2O
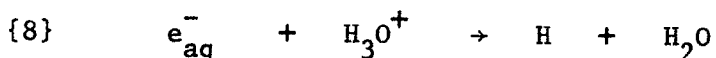
The yield expression for H_2O_2 reduction in acid solution is almost identical to equation {54}.

{54a}
$$G(-H_2O_2) = \left[\left(G_H + G_{e_{aq}^-}\right)\left\{\frac{k_{50}(k_{30} + k_{37})}{k_{37}(k_{50} + k_{51})}\right\} + \frac{k_{30}}{k_{37}}\left(G_{e_{aq}^-} + G_{OH}\right) - G_{H_2O_2} \right]$$
$$+ \left(1 + \frac{k_{30}}{k_{37}} \ k_{52}\right)\left(\frac{G_{e_{aq}^-} + G_H + G_{OH}}{2 \ k_{53} \ D}\right)^{\frac{1}{2}} \ [(CH_3)_2CHOH]$$

In the low dose rate studies, a reduction in the yield of acetone was observed on increasing the concentration of hydrogen peroxide (Table 3.2) suggesting that a reaction such as {57} may be the competing first order termination process.

{57} H_2O_2 + $CH_3(\overset{\bullet}{C}H_2)CHOH$ → $(CH_3)_2CHOH$ + HO_2
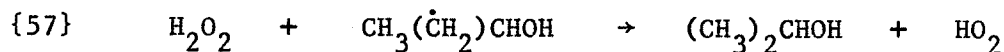
Subsequent reactions of the HO_2 radical would cause inhibition

and a reduction in the yield of acetone.

1.0 M – Pure 2-Propanol / 0.01 M H_2O_2

As the concentration of 2-propanol is increased to values greater than 1.0 M the yield of acetone increases less rapidly reaching a maximum of G(Acetone) ∿100 in the region of 3.7 M (Fig.3.5). This levelling off in the yield of acetone could be attributed to the increasing rate of reaction {52} with increasing alcohol concentration. If reaction {52} becomes sufficiently rapid it may no longer be exclusively rate controlling and the chain length would be determined in part by competition between reactions {31} and {38}.

{31}   I + H_2O_2 → $(CH_3)_2CO$ + H_2O + OH

{38}   2 I → $(CH_3)_2CO$ + $(CH_3)_2CHOH$
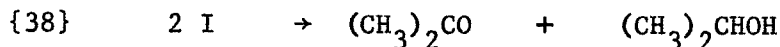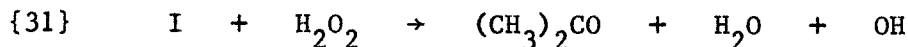
This would result in a transition to a situation in which the

reaction becomes independent of alcohol concentration and first order in hydrogen peroxide. In fact, in this region, the yield-dose curve for hydrogen peroxide reduction becomes non-linear although at none of the higher alcohol concentrations is it completely first order.

At alcohol concentrations in excess of 4.0 M the chain yield of acetone decreases to a limiting value of 16.3 ± 1.0 in pure 2-propanol. There are at least two possible explanations for this decrease. The argument presented above suggests that, with increasing alcohol concentration, the yield should increase to a maximum limiting value and then remain constant. This assumes, however, that the primary yields of free radical intermediates remain unchanged which is highly improbable as the system is changed from pure water as solvent to pure 2-propanol. A decrease in the primary yields with increasing alcohol concentration may cause a decrease in the acetone yields. However, it is highly unlikely that the primary yields would change sufficiently to account for such a marked decrease in G(Acetone).

In a study of the photoinduced reaction Barrett et al.(26) found an almost identical change in the quantum yield for hydrogen peroxide reduction although the primary quantum yield of peroxide homolysis is said to remain constant in this concentration range. The decreasing yield was attributed by Barrett to reaction of the product OH radicals with alcohol molecules in the "primary photochemical cage". The parallel between the radiation chemical results reported here and the photochemical results makes this explanation unlikely since the radiation chemical "spur" is not analogous to the photochemical "cage".

It is proposed that with increasing 2-propanol concentration, and consequent increase in the rate of reaction {52}, reaction {31} becomes the principal rate controlling propagation step. The decrease in G(Acetone) results from the effect of the decreasing dielectric constant of the medium on the formation

of a polar transition state in reaction {31}. This reaction may
be thought of as an electrophilic substitution reaction of the
organic radical with an H_2O_2 molecule.

$$\{31\} \qquad HO-\underset{\overset{|}{CH_3}}{\overset{CH_3}{C}}\!\cdot\ (\delta+)\ +\ (\delta-)\ O\!\!\begin{array}{c}\overset{H}{\diagdown}\\ \diagup\\ \diagdown H\end{array}\ \rightarrow\ HO\cdots\underset{\overset{\Delta}{CH_3}}{\overset{CH_3}{C}}\cdots OH\ +\ OH$$
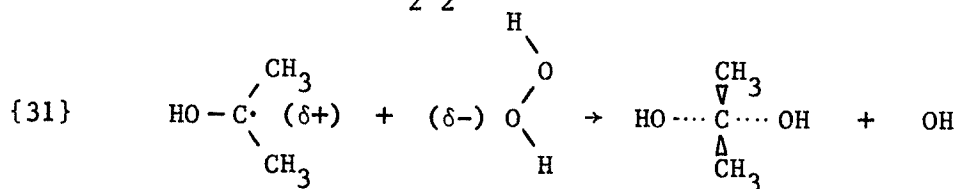
The reaction of the polar radical I with the polar molecule H_2O_2
would involve the formation of a polar transition state. However,
it is known that with decreasing dielectric constant the rate of
reaction between two dipoles decreases (49). Therefore at high
alcohol concentrations the activation energy of formation of the
polar transition state increases and hence the rate of the
propagating reaction {31} and with it the chain yield is reduced.

At high 2-propanol concentrations there is a significant
dose rate effect on the yields of acetone (Table 3.3). Although
this dose rate effect approaches, but never equals, a simple
inverse square root dependence, the evidence supports the
suggestion that reaction {31} is the main rate controlling
propagation reaction at high alcohol concentrations. The absence
of clear cut dose rate data suggests that mixed termination is
occurring in concentrated 2-propanol solutions.

Sherman (50) has reported the formation of methane and
acetic acid in chain yields in addition to acetone in the radiation
induced oxidation of alkaline 2-propanol by nitrous oxide. The
formation of methane and acetic acid was accounted for by the
stoichiometric reaction,

$$\{58\} \qquad (CH_3)_2CHOH\ +\ N_2O\ \rightarrow\ CH_3CO_2H\ +\ N_2\ +\ CH_4$$
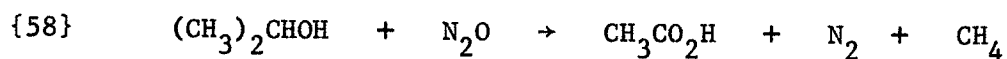
No chain formation of methane has been observed in the oxidation
of neutral aqueous solutions of 2-propanol by H_2O_2, thus
discounting the possibility of a reaction analogous to {58} with H_2O_2.

0.52 M 2-Propanol / $<10^{-3}$ M H_2O_2
_____

At a constant concentration of 2-propanol (0.52 M), the rate of peroxide removal below 10^{-3} M H_2O_2 becomes dependent on its concentration (Fig.3.6) and becomes essentially first order in H_2O_2 below 10^{-4} M. This indicates that the rate of reaction {31} has become sufficiently slow to become rate determining at these low peroxide concentrations.

When the concentration of H_2O_2 reaches its steady-state value the requirement of oxidation-reduction balance in the system predicts that,

{59}   G(Net oxidation) = G(Net reduction)

{60} $G(Acetone) = G(H_2) = G_{H_2} + G_H$

This latter value is expected to be of the order of 1.0 (13) in good agreement with the experimental value of G(Acetone) = 0.97 ± 0.05. The magnitude of the steady-state concentration of H_2O_2 could be used to determine the relative rates of the terminating and propagating reactions but as stated before this quantity was found to be rather irreproducible.

3.3 Further Work

It has been established that abstraction of hydrogen atoms from 2-propanol by OH radicals is less specific as to the site of reaction than previously believed. Also, the presence of two distinct alcohol derived radical species has been demonstrated to have unusual mechanistic and kinetic implications for the oxidation of 2-propanol by H_2O_2. A new mechanism was therefore proposed for the oxidation of 2-propanol.

It is now desirable to establish the generality of this mechanism. In order to do this it was decided to compare the

effect of γ-radiation on the oxidation of aqueous ethanol solutions, where formation of two distinct solute derived radicals is possible, and the effect of γ-radiation on the oxidation of aqueous methanol solutions where only one solute-derived radical species can be formed.

The oxidation of ethanol should be analogous to the oxidation of 2-propanol. A contrast should be observed in the oxidation of methanol. The results of these investigations are presented in the following section.

4. RESULTS AND DISCUSSION – ETHANOL AND METHANOL

4.1 Results

The γ-radiation induced oxidation of ethanol and methanol in deaerated aqueous solutions by hydrogen peroxide has been investigated. Results from these studies are discussed below.

Ethanol / H_2O_2

The hydrogen peroxide removal yield in the presence of a constant concentration of ethanol (1.71 M) is shown in a dose-yield plot, Fig.4.1. The figure is a composite graph compiled from several runs with different starting concentrations of hydrogen peroxide. The yield is independent of hydrogen peroxide concentration in the range 5×10^{-2} M to 5×10^{-3} M H_2O_2.

All dose-yield plots for peroxide removal are linear allowing accurate calculation of $G(-H_2O_2)$ values. A typical dose-yield plot is illustrated in Fig.4.2. The stoichiometric equivalence of peroxide removal and acetaldehyde formation is clearly demonstrated in the same figure. For the particular concentration of ethanol used (0.085 M), $G(-H_2O_2) = 46.6 \pm 1.5$ and $G(CH_3CHO) = 46.8 \pm 1.5$. Additional $G(-H_2O_2)$ and $G(CH_3CHO)$ yields obtained at several different concentrations of ethanol are tabulated in Table 4.1.

The peroxide removal yields and acetaldehyde formation yields are linearly dependent on the concentration of ethanol in the range 0.08 M to 0.9 M ethanol. This linear dependence of yields on ethanol concentration is demonstrated in Fig.4.3. Extrapolation of both yields as shown in Fig.4.3 produces the following results,

Fig.4.1

Dose-yield plot for H_2O_2 removal.
[Ethanol] = 1.71 M.
Initial [H_2O_2]: (O) 5×10^{-2} M
(●) 2×10^{-2} M
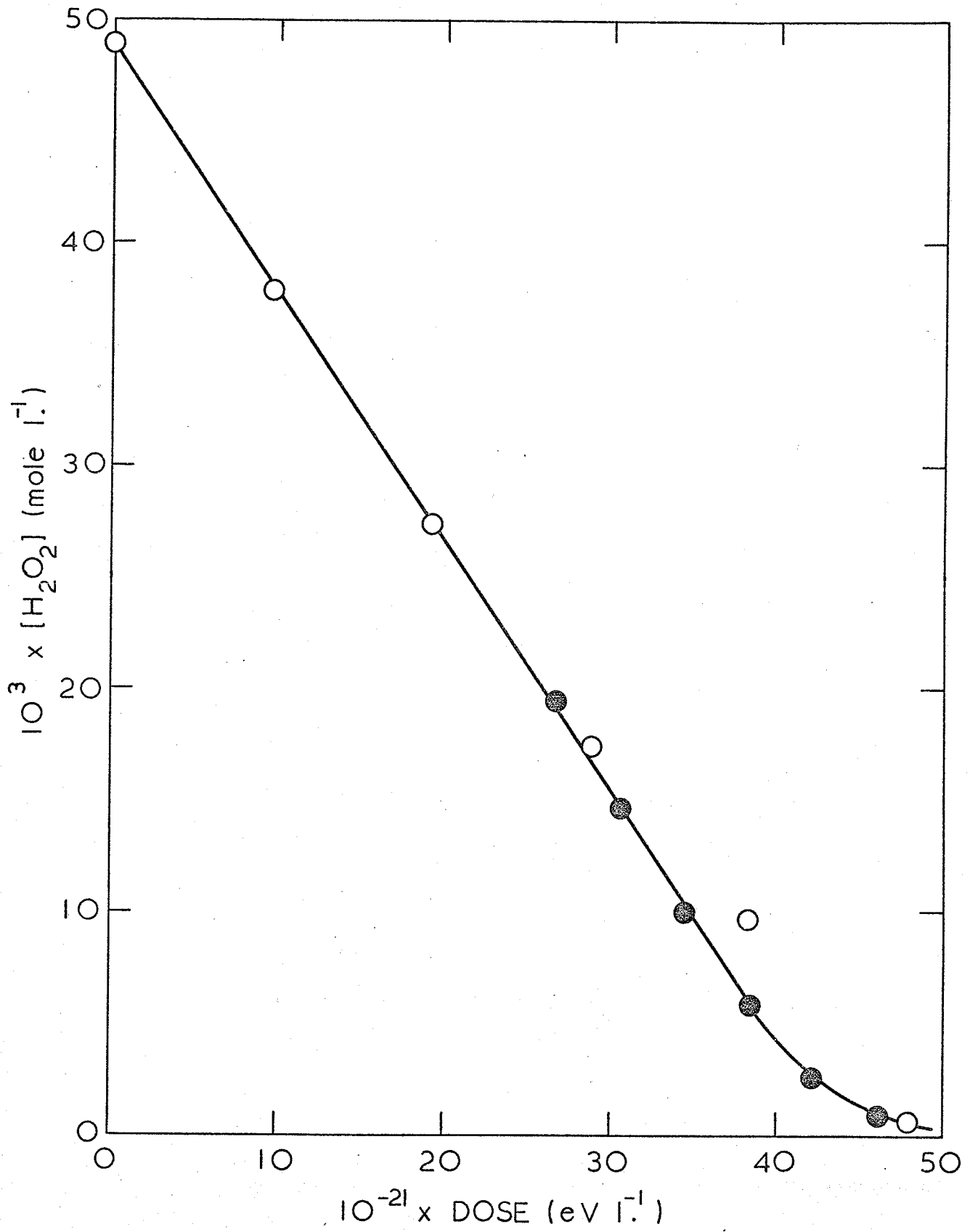
Fig.4.2

Dose-yield plot for H_2O_2 removal and CH_3CHO

formation. [Ethanol] = 0.085 M.

Initial $[H_2O_2]$ = 2 x 10^{-2} M

    (O) H_2O_2 removal

    (●) CH_3CHO formation

(56a)
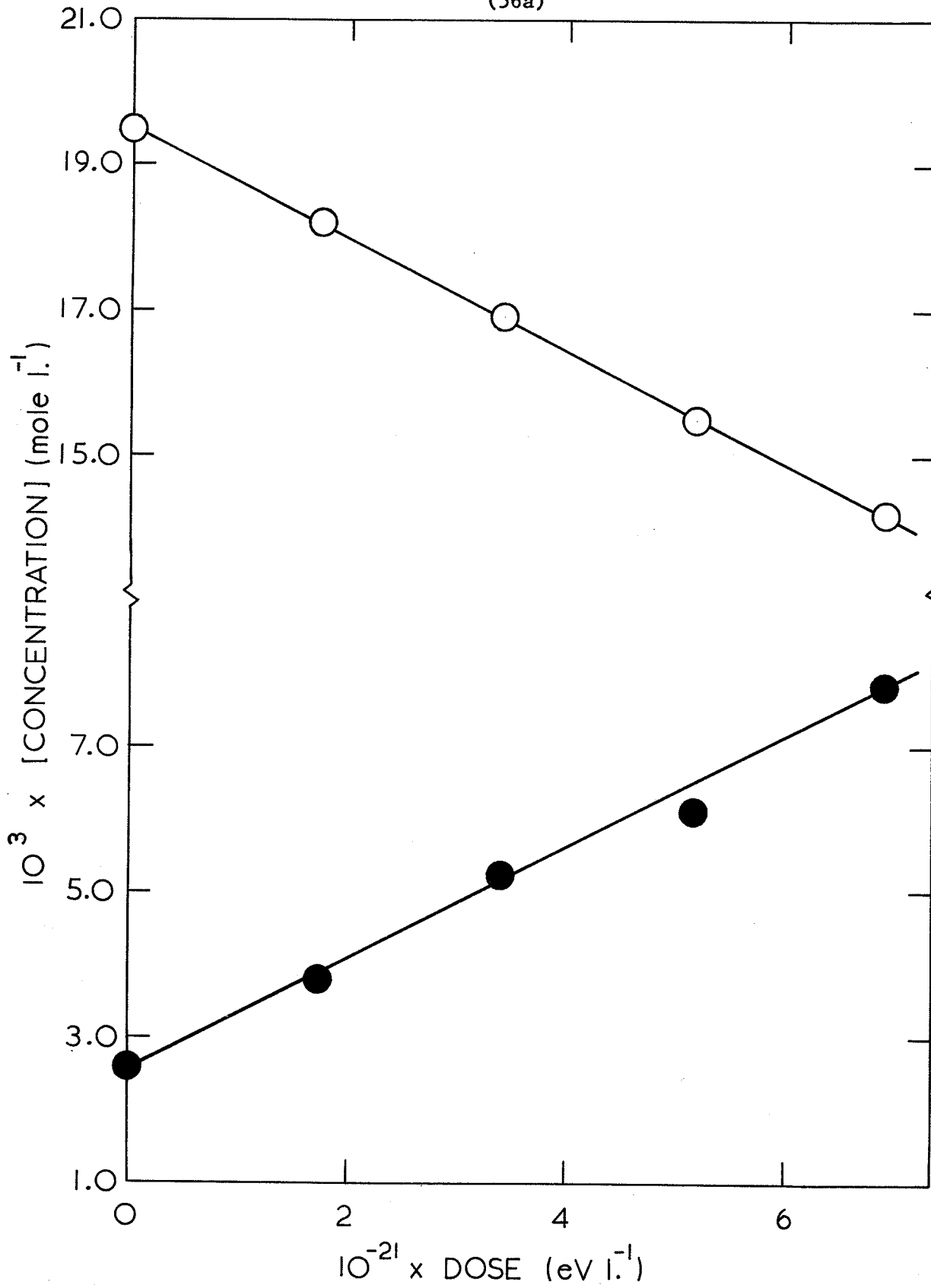
Fig.4.3

Plot of $G(-H_2O_2)$ and $G(CH_3CHO)$ against
[Ethanol]. Dose Rate = 1.48×10^{19} eV 1^{-1} s^{-1}.

(○) $G(-H_2O_2)$
(●) $G(CH_3CHO)$

(57a)
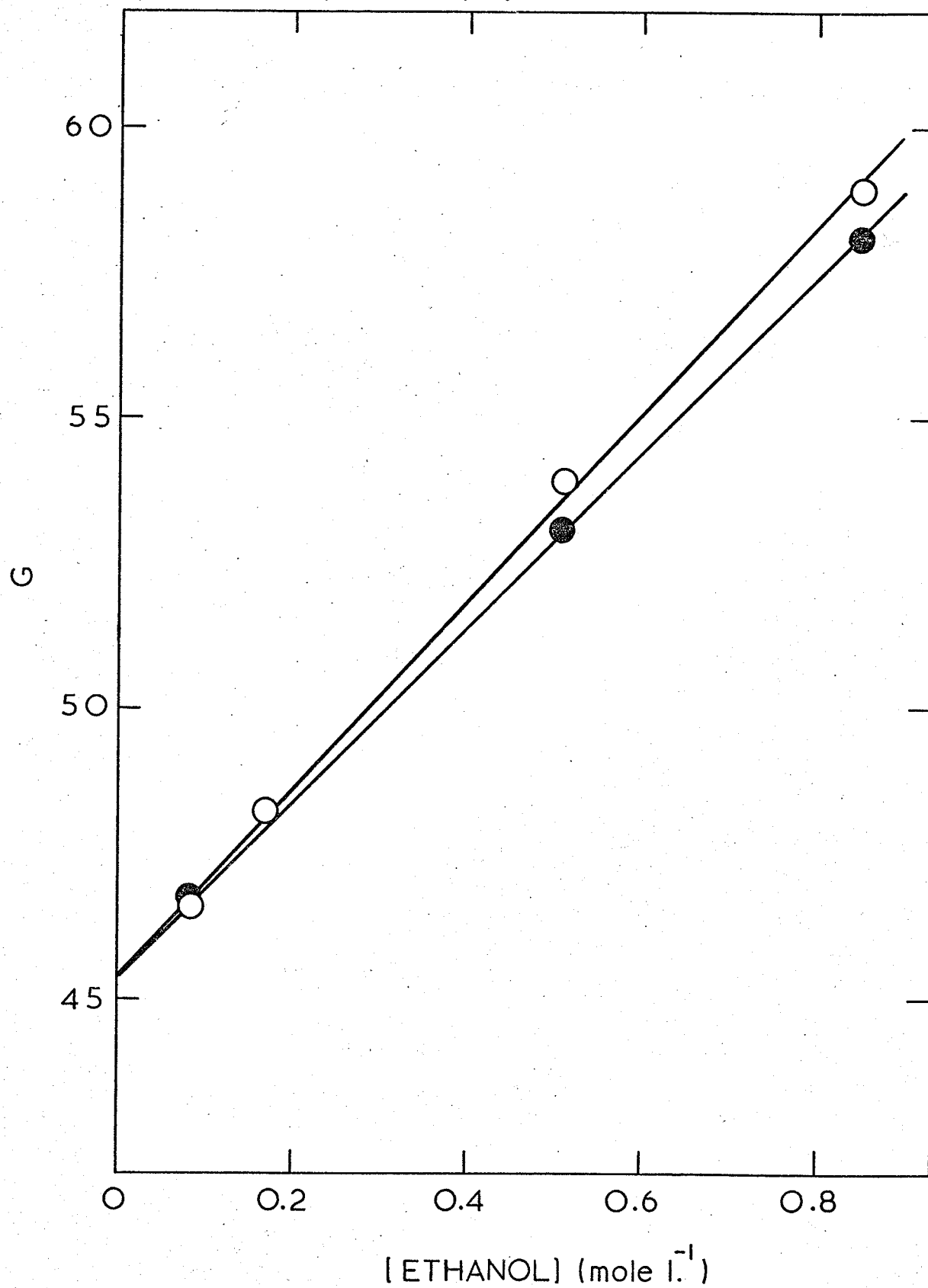
[ETHANOL] (mole l.$^{-1}$)

TABLE 4.1

$G(-H_2O_2)$ and $G(CH_3CHO)$ yields at various
ethanol concentrations. Initial $[H_2O_2] = 2 \times 10^{-2}$ M.

[Ethanol]		$G(-H_2O_2)$	$G(CH_3CHO)$
mole l^{-1}	mole %		
0.085	0.15	46.6	46.8
0.17	0.31	48.2	
0.51	0.94	53.9	53.1
0.85	1.60	58.9	58.1
1.71	3.3	65.1	
3.43	7.0	74.7	
8.57	22.4	52.1	
Pure Ethanol	100	18.2	

$G^o(-H_2O_2) = 45.4 \pm 1.5$ and $G^o(CH_3CHO) = 45.5 \pm 1.5$ at zero ethanol concentration, indicating the presence of a large alcohol independent chain term. The linear dependence of yields on ethanol concentration does not hold for concentrations greater than 1 M ethanol.

The effect of altering the dose rate on the chain removal of hydrogen peroxide for a constant ethanol concentration is shown in Fig.4.4. $G(-H_2O_2)$ yields are plotted against $(1/D)^{\frac{1}{2}}$ where D is the dose rate in eV l^{-1} s^{-1}. The results are also tabulated in Table 4.2. Fig.4.4 clearly shows that there is a dependence of $G(-H_2O_2)$ on $(1/D)^{\frac{1}{2}}$.

Peroxide removal yields were obtained over a wide range of ethanol concentrations. The yields are compiled in Table 4.1.

Fig.4.4

Plot of $G(-H_2O_2)$ against $(1/D)^{\frac{1}{2}}$.
[Ethanol] = 0.51 M.

The y-axis is labeled $G(-H_2O_2)$ with values 45, 50, 55, 60, 65.

The x-axis is labeled $10^{10} \times \left(\frac{1}{D}\right)^{1/2} (eV\ l.^{-1}\ sec.^{-1})^{-1/2}$ with values 0, 2, 4, 6, 8.
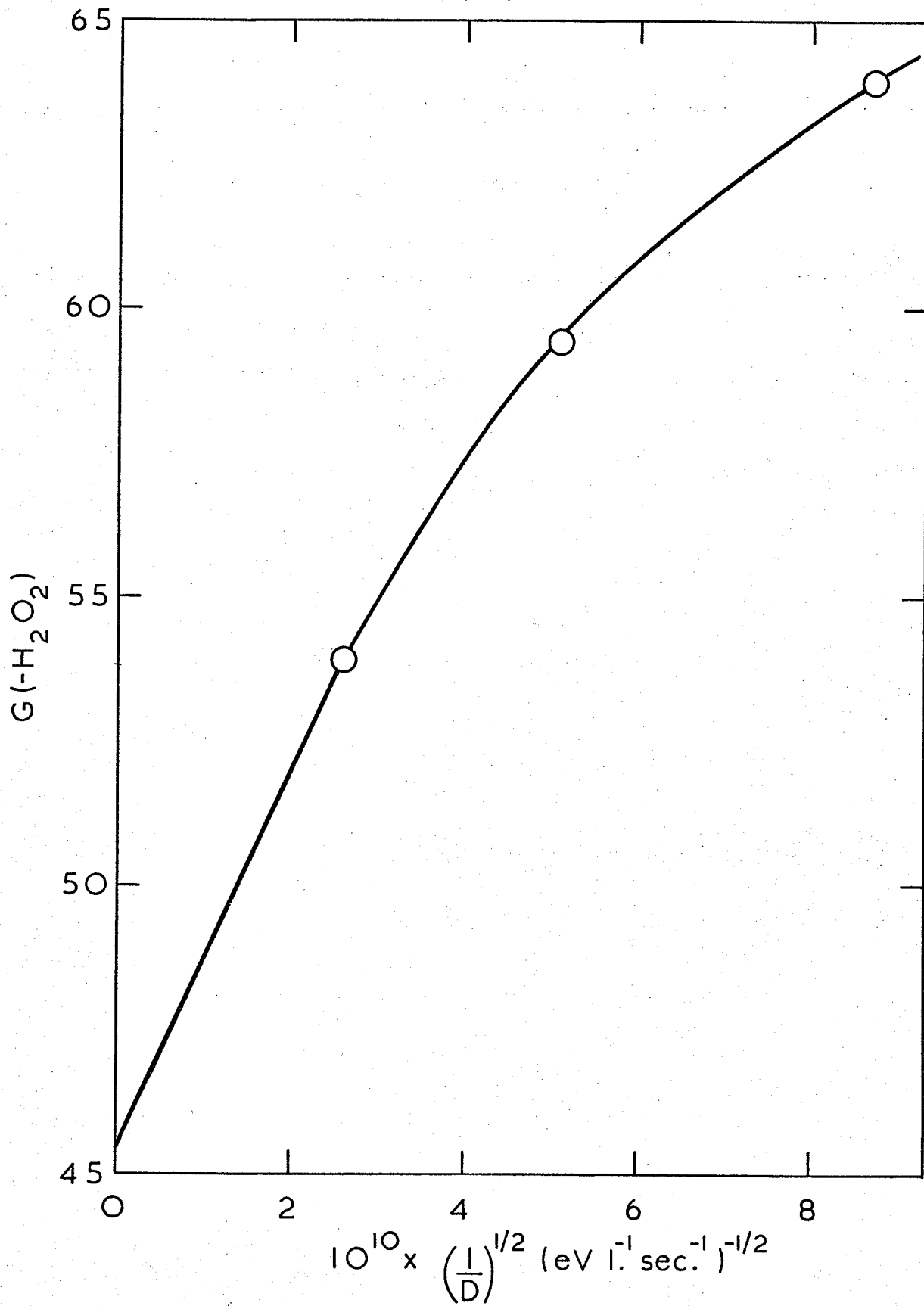
TABLE 4.2

Dose rate effect: $G(-H_2O_2)$ yields at

various values of $(1/D)^{\frac{1}{2}}$. [Ethanol] = 0.51 M.

Initial $[H_2O_2]$ = 2 x 10^{-2} M.

10^{10} x $(1/D)^{\frac{1}{2}}$ (eV 1^{-1} s^{-1})$^{-\frac{1}{2}}$	$G(-H_2O_2)$
2.60	53.9
5.10	59.4
8.70	63.9

The $G(-H_2O_2)$ yields are also plotted against mole percent ethanol in Fig.4.5. From Fig.4.5 it is seen that $G(-H_2O_2)$ increases with increasing mole percent ethanol reaching a maximum value of ∿75 at a concentration in the region of 3.4 M ethanol (7%). As the ethanol concentration is increased above 3.4 M, $G(-H_2O_2)$ decreases to a limiting value of 18.2 ± 1.0 in pure ethanol solution.

Below 5 x 10^{-3} M H_2O_2 the rate of peroxide removal is dependent on hydrogen peroxide concentration as shown in the dose-yield plot, Fig.4.6. The figure is a composite curve made up of results from runs with three different starting concentrations of hydrogen peroxide and using a constant ethanol concentration (0.51 M). Hydrogen peroxide is removed until a steady-state value of ∿3 x 10^{-7} M H_2O_2 is reached.

Methanol / H_2O_2

Hydrogen peroxide is removed and formaldehyde is formed in

Fig.4.5

Plot of $G(-H_2O_2)$ yields against mole percent
alcohol.

      (O) Ethanol

      (●) Methanol

Initial $G(-H_2O_2)$ values are used in the case
of methanol.
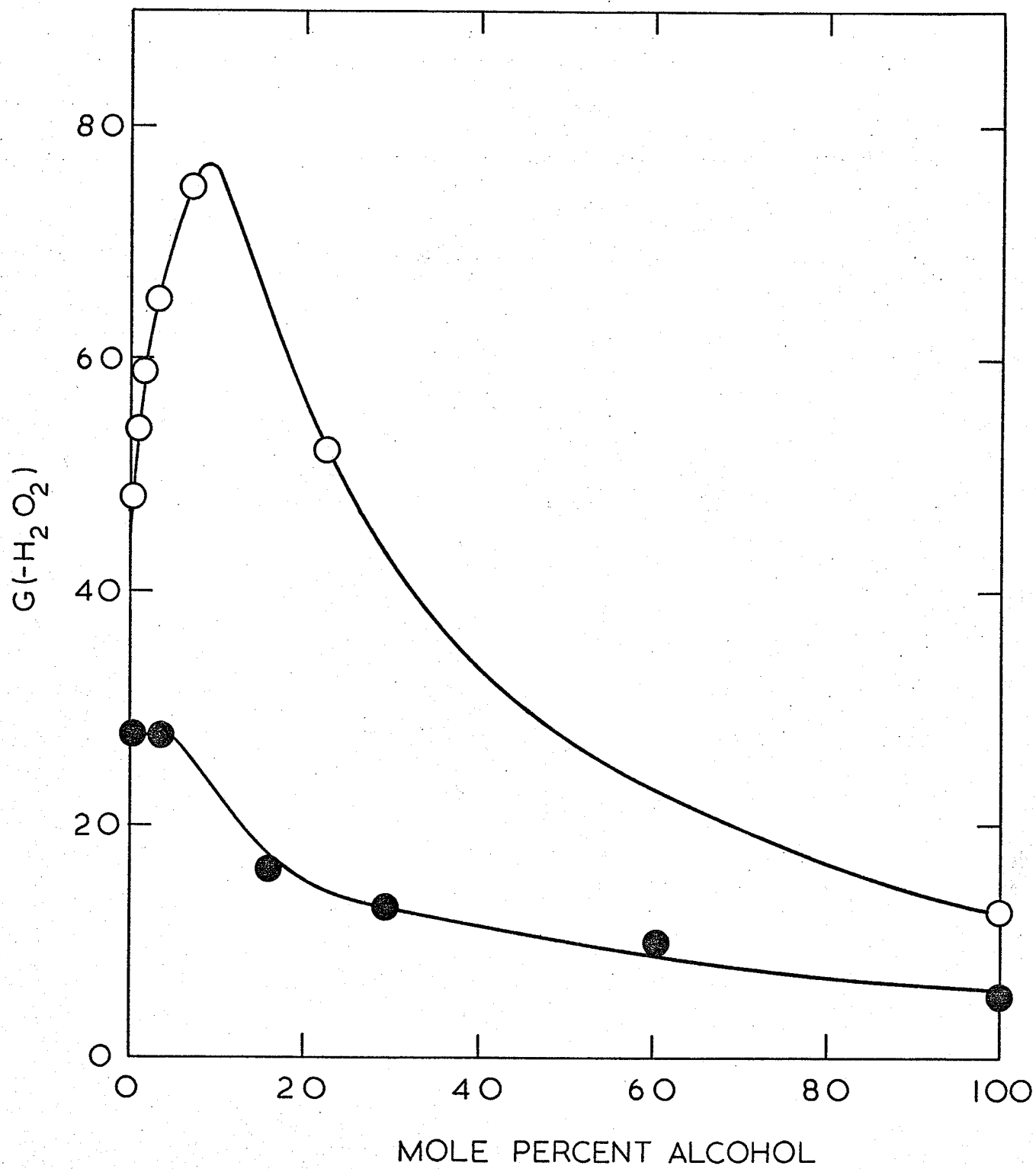
Fig.4.6

Dose-yield plot for H_2O_2 removal.

[Ethanol] = 0.51 M.

Initial [H_2O_2] : (●) 2.5 x 10^{-3} M

(O) 10^{-3} M

(▲) 10^{-4} M
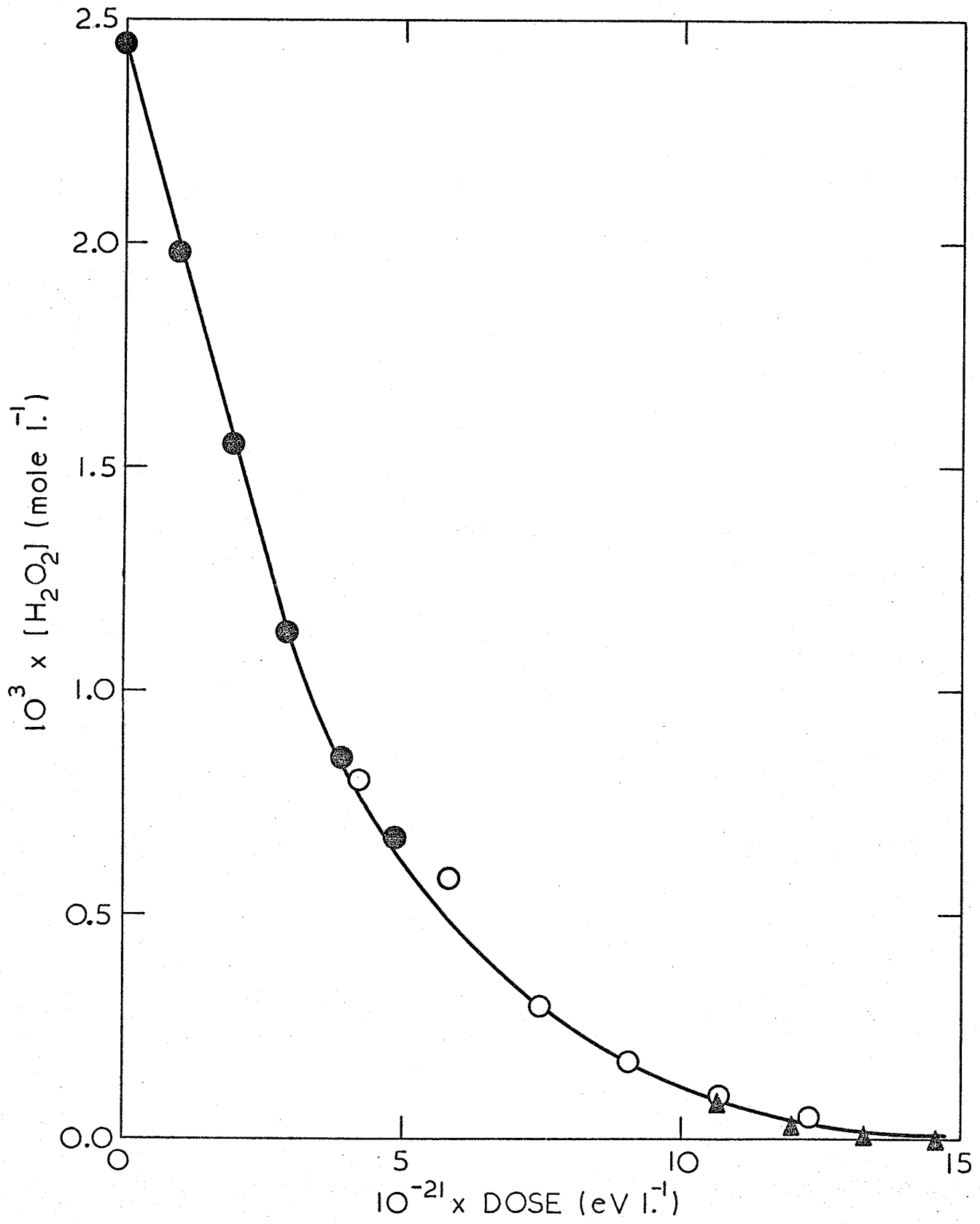
stoichiometrically equivalent chain quantities. For a particular concentration of methanol (0.13 M) this stoichiometric equivalence is graphically illustrated in Fig.4.7.

The rate of peroxide removal shows a first order dependence on hydrogen peroxide concentration over a wide range of methanol concentration. A typical plot of $\log[H_2O_2]$ against irradiation time is seen in Fig.4.8. From the slope of the straight line in this graph an apparent first order rate constant for peroxide removal can be calculated. First order rate constants for peroxide removal have been determined for several different concentrations of methanol. The rate constants are tabulated in Table 4.3. Within experimental error, the apparent first order rate constant for peroxide removal is constant over the range 0.1 M to 2.0 M methanol.

TABLE 4.3

Apparent first order rate constants for

H_2O_2 removal at different methanol concentrations.
Initial $[H_2O_2]$ = 10^{-2} M.

$[CH_3OH]$ (mole l^{-1})	10^{-19} x Dose Rate (eV l^{-1} s^{-1})	10^4 x $k_{app.}$ (s^{-1})
0.13	1.60	8.9
0.49	1.60	9.6
0.99	1.60	9.9
0.99	0.43	4.5
1.98	1.60	9.5

Fig.4.8 and Table 4.3 both illustrate the effect of altering the dose rate. The rate of removal of peroxide shows a square root

Fig.4.7

Dose-yield plot for H_2O_2 removal and HCHO
formation. [Methanol] = 0.125 M.
Initial $[H_2O_2] = 10^{-2}$ M.

    (O) H_2O_2 removal

    (●) HCHO formation

(64a)
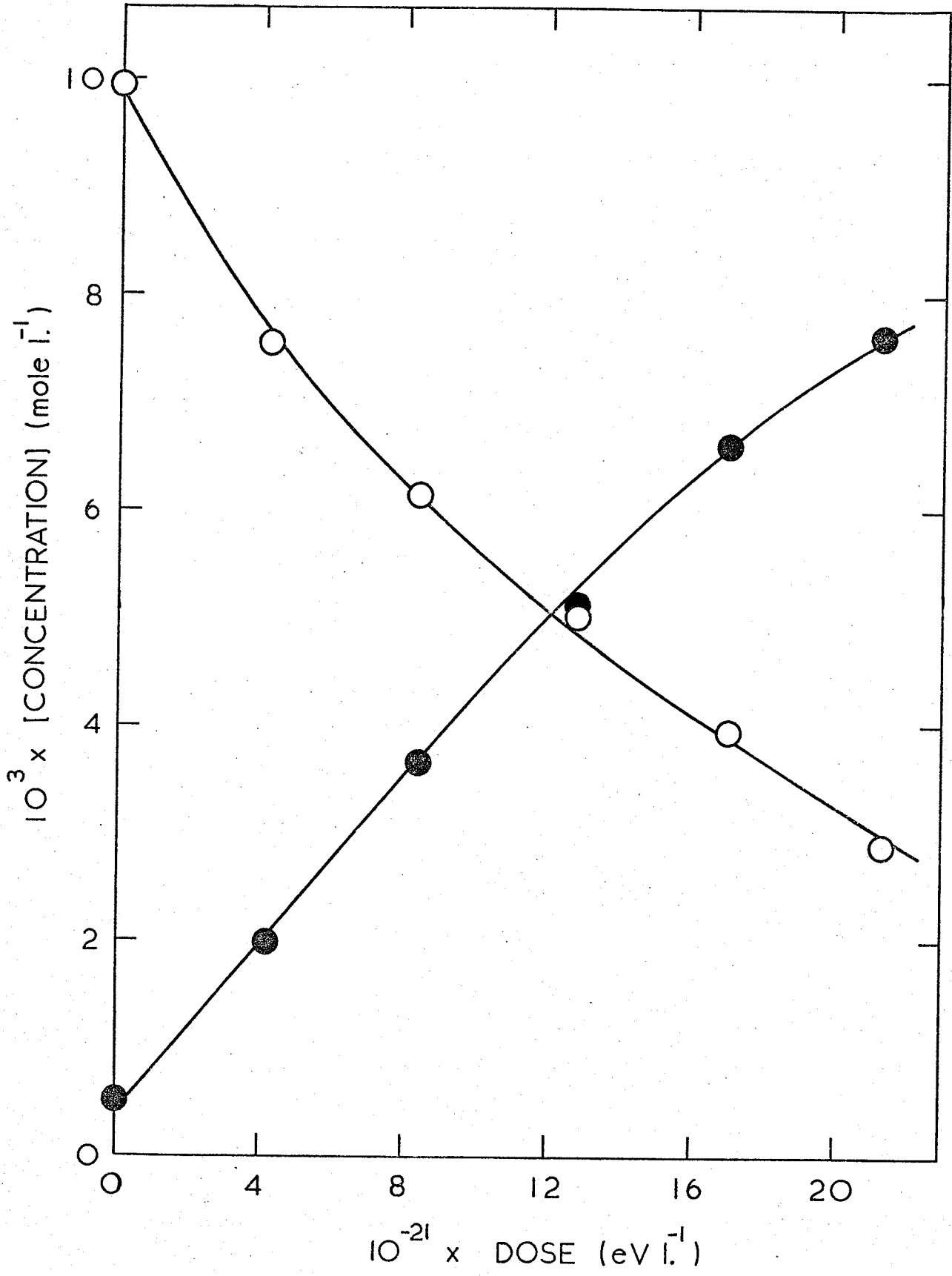
Fig.4.8

Plot of log $[H_2O_2]$ against time for H_2O_2

removal. $[Methanol]$ = 0.99 M.
Initial $[H_2O_2]$ = 10^{-2} M.

(O) Normal dose rate

(●) Attenuation to 26 %
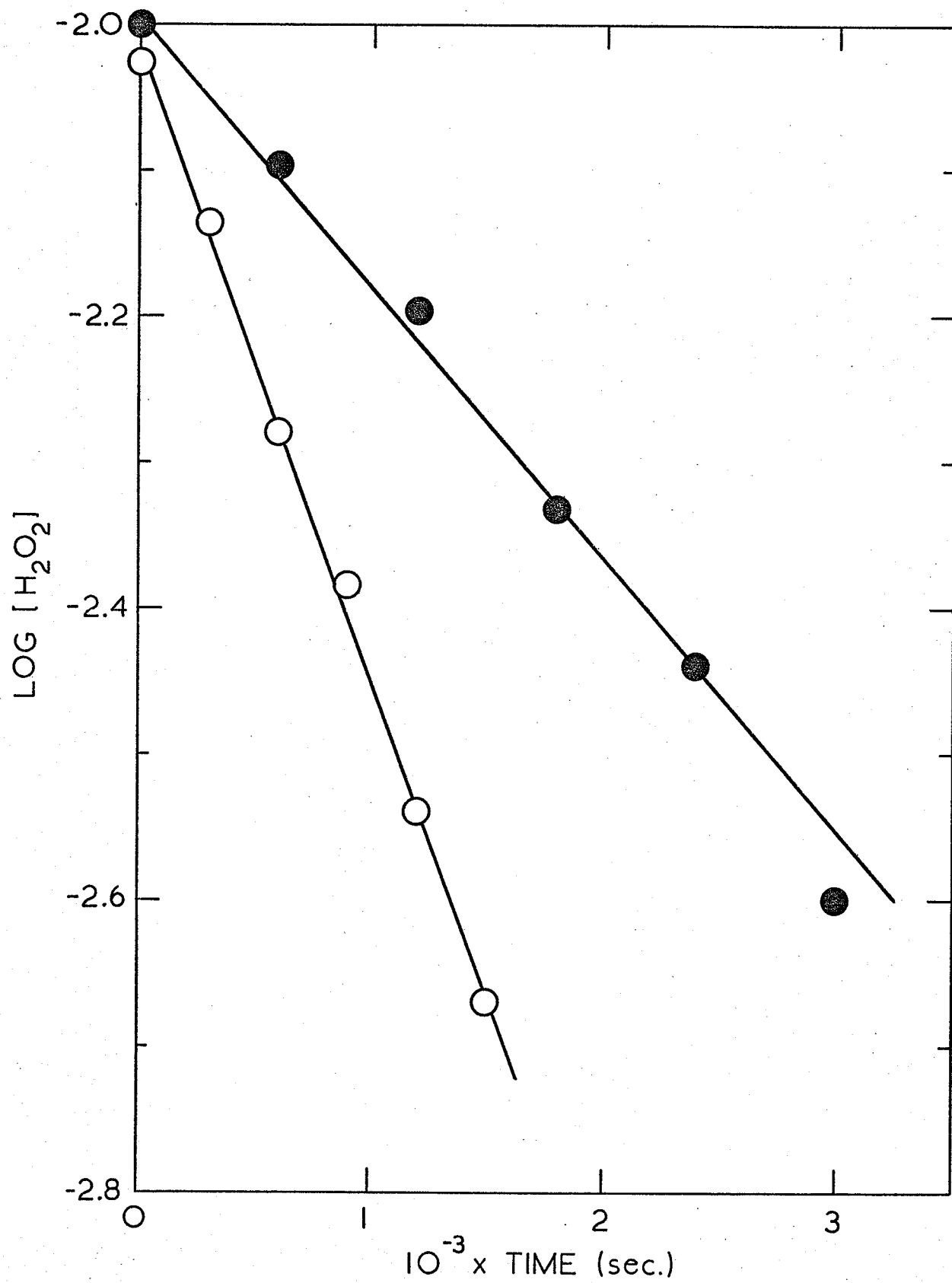
dependence on the dose rate.

Initial $G(-H_2O_2)$ yields are independent of methanol concentration in the range 0.1 M to 2.0 M methanol as shown in Fig.4.5. Initial $G(-H_2O_2)$ yields only can be used because of the dependence of yields on hydrogen peroxide concentration. In Fig.4.5, as the mole percentage of methanol is increased above ~7%, initial $G(-H_2O_2)$ yields decrease gradually to a limiting value of 5.0 ± 0.5 in pure methanol. Initial $G(-H_2O_2)$ yields at various methanol concentrations are compiled in Table 4.4.

TABLE 4.4

Initial $G(-H_2O_2)$ yields at various

concentrations of methanol.

Initial $[H_2O_2] = 10^{-2}$ M.

[MeOH]		Initial $G(-H_2O_2)$
mole 1^{-1}	mole%	
0.49	0.89	27.8
0.99	1.82	27.0
1.98	3.72	27.0
7.35	15.5	16.2
12.35	29.4	12.9
19.76	60.7	9.9
Pure Methanol	100	5.0

4.2 Discussion

0.085 - 3.0 M Ethanol / 5 x 10^{-2} - 5 x 10^{-3} M H_2O_2

The results from the chain oxidation of ethanol compare favourably with the results associated with the chain oxidation of 2-propanol in similar concentration regions.

As discussed previously, 2-propanol was oxidized to acetone and hydrogen peroxide was removed in stoichiometrically equivalent chain yields. The yields were independent of hydrogen peroxide concentration in the range 5 x 10^{-2} M to 10^{-3} M H_2O_2 and linearly dependent on 2-propanol concentration in the range 0.13 M to 1.05 M 2-propanol. The plot of G v. [2-Propanol] extrapolated to a large positive intercept at zero alcohol concentration. The yields showed an unusual dose rate effect.

For ethanol, it is observed that the peroxide removal yields are independent of peroxide concentration in the range 5 x 10^{-2} M to 5 x 10^{-3} M H_2O_2 and linearly dependent on ethanol concentration in the range 0.08 to 0.85 M ethanol. Extrapolation of the G v. [Ethanol] plot yields a large positive intercept at zero alcohol concentration indicating a large alcohol independent chain yield. A dose rate effect on the yields is noted.

The mechanism proposed to account for the effects observed in aqueous 2-propanol solutions can be used to explain the results in aqueous ethanol solutions. The proposed mechanism follows:

{13} $H_2O \rightsquigarrow e_{aq}^-$, H, OH, H_3O^+, H_2O_2, H_2

{39} $e_{aq}^- + H_2O_2 \rightarrow OH + OH^-$

{40} $H + CH_3CH_2OH \rightarrow H_2 + CH_3\dot{C}HOH$

{61} $H + CH_3CH_2OH \rightarrow H_2 + \cdot CH_2CH_2OH$

{34} $OH + CH_3CH_2OH \rightarrow H_2O + CH_3\dot{C}HOH$

{62} OH + CH_3CH_2OH → H_2O + $\cdot CH_2CH_2OH$

{35} H_2O_2 + $CH_3\dot{C}HOH$ → CH_3CHO + OH + H_2O

{63} $\cdot CH_2CH_2OH$ + CH_3CH_2OH → CH_3CH_2OH + $CH_3\dot{C}HOH$

{64} $2 \cdot CH_2CH_2OH$ →   1,4-Butanediol, or CH_3CHO + CH_3CH_2OH
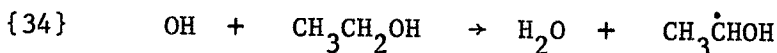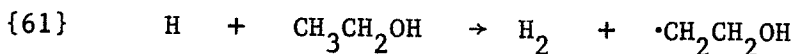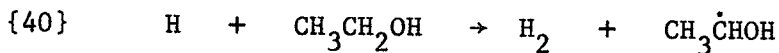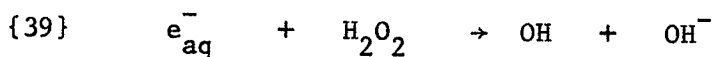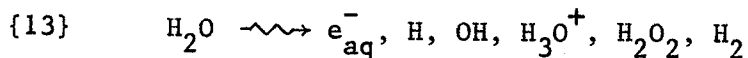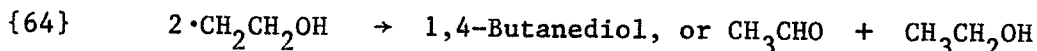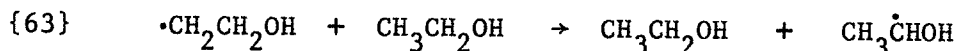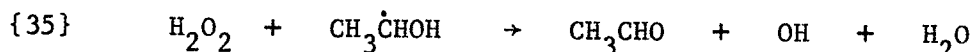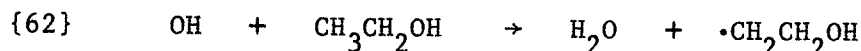
Arguments for the inclusion of reactions {61}, {62}, {63} and {64} are briefly discussed below:

Hydrogen atoms have been shown to abstract β-hydrogens from ethanol (51). A value for the rate constant ratio k_{40}/k_{61} =12.6 was determined. Therefore reaction {61} must be included in the mechanism.

Considerable evidence has been presented in the preceding chapter that OH radicals readily abstract β-hydrogens from 2-propanol (27,43). Similar evidence may be used to support the conclusion that OH radicals readily abstract β-hydrogens from ethanol. The ESR spectrum of $\cdot CH_2CH_2OH$ was observed upon photolyzing solutions of ethanol and water containing 1% H_2O_2 (43). Adams and Willson (47) conclude from pulse radiolysis studies on the oxidation of organic radicals in aqueous solution, that the percentage of OH attack at the α-carbon in ethanol is 97%. Hence reaction {62} must be included in the mechanism.

The analogue of the hydrogen atom transfer reaction {63} in 2-propanol has been fully discussed in the previous chapter. Supporting evidence for reaction {63} comes from ESR work. The intensity of the ESR spectrum of $\cdot CH_2CH_2OH$ observed by Livingston and Zeldes (43) was enhanced on increasing the relative percentage of water, implying that reaction {63} is occurring. Reaction {63} is the rate controlling step in the mechanism.

The exclusion of a reaction of the β-radical, $\cdot CH_2CH_2OH$, with H_2O_2 in an oxidative step is supported partly by the observation that the β-radical is much less reactive as a reductant (47) and partly by the ESR evidence of Norman and West (22) who observe that the radical $CH_3\dot{C}HOH$ reduces H_2O_2 much more readily

than $\cdot CH_2CH_2OH$.

Reaction {63} is in competition with the termination reaction {64}. 1,4-Butanediol was tentatively identified as a reaction product using vapour phase chromatography.

On the basis of the proposed mechanism an expression for the yield of H_2O_2 removal can be derived.

$$\{65\} \qquad G(-H_2O_2) = \left[G_{e^-_{aq}} - G_{H_2O_2} + \left\{ G_H \frac{k_{40}(k_{34} + k_{62})}{k_{62}(k_{40} + k_{61})} \right\} + \frac{k_{34}}{k_{62}}(G_{e^-_{aq}} + G_{OH}) \right]$$

$$+ \left(\frac{1 + \dfrac{k_{34}}{k_{62}}}{} \right) k_{63} \left(\frac{G_{e^-_{aq}} + G_H + G_{OH}}{2 \, k_{64} \, D} \right)^{\frac{1}{2}} [CH_3CH_2OH]$$

(D is the dose rate in units of 6.02×10^{25} eV 1^{-1} s^{-1})

A similar expression may be derived for $G(CH_3CHO)$ which differs only in the initial non-chain term, $G_{e^-_{aq}} - G_{H_2O_2}$, which depends upon the exact stoichiometry of the terminating reaction {64}.

The form of this yield expression is in excellent agreement with the experimental results. The portion of the yield expression in square brackets represents a large alcohol independent chain yield and therefore also represents the intercept obtained on extrapolation of Fig.4.3 to zero alcohol concentration. A value for the rate constant ratio k_{34}/k_{62} may be determined from this expression. Using $G^o(-H_2O_2) = 45.4$ at zero ethanol concentration and the values of $G_{e^-_{aq}}$, G_H, G_{OH}, $G_{H_2O_2}$ (13) cited in the previous chapter and assuming values for k_{40}, k_{61}, $k_{34} + k_{62}$ (14),

$$k_{40} = 1.6 \times 10^7 \, M^{-1} \, s^{-1}$$

$$k_{61} = 1.7 \times 10^6 \, M^{-1} \, s^{-1}$$

$$k_{34} + k_{62} = 1.1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$$

the ratio k_{34}/k_{62}, the relative probability of abstraction by OH
from the α- and β-positions in ethanol, is found to be 8.6. This
may be compared to the estimate of 6.2 for the analogous ratio
when 2-propanol is the substrate. Adams and Willson (47) have
estimated that 97% and 95% of the radicals formed by OH attack
on ethanol and 2-propanol respectively are the result of attack
at the α-position, whereas the rate constant ratios found in this
work correspond to 90% and 86% α-attack. These percentages are
significantly lower than those found by Adams and Willson.

The value of 97% attack by OH at the α-position of ethanol
corresponds to a ratio of $k_{34}/k_{62} = 32.3$ (47). However, Lifshitz
and Stein (51) quote a value for the relative probability of
abstraction by H from the α- and β-positions of ethanol, of
$k_{40}/k_{61} = 12.6$. Based solely on the relative exothermicities of
hydrogen atom abstraction reactions by H and OH, one would expect
that the relative probability of abstraction by OH from the α-
and β-positions in ethanol would be less than 12.6, that is,
hydrogen abstraction by OH radicals is less selective than hydrogen
abstraction by H. The value of $k_{34}/k_{62} = 8.6$ derived in this work
agrees with the above argument. Therefore, the figures obtained
by Adams and Willson (47) for percentage attack at α-positions
of various solutes by OH must be regarded as upper limits.

Using $k_{34}/k_{62} = 8.6$ and assuming $k_{34} + k_{62} = 1.1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$
(14) gives:

$$k_{34} = 1.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$$

$$k_{62} = 1.1 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$$

These may be compared with the values of the corresponding rate
constants for 2-propanol.

$$k_{30} = 1.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$$

$$k_{37} = 2.0 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$$

The second part of the yield expression predicts, as observed experimentally, a linear dependence of the $G(-H_2O_2)$ yield on ethanol concentration and the coefficient of the alcohol concentration term includes a reciprocal square root dependence on dose rate. A plot of $G(-H_2O_2)$ against $(1/D)^{\frac{1}{2}}$ should be linear and at extremely high dose rates should extrapolate to a finite value of $G^o(-H_2O_2) = 45.4$ at zero ethanol concentration. As shown in Fig.4.4, the system displays a significant dose rate dependence although it is not a simple square root relationship. A dose rate effect implies that termination by the bimolecular process {64} is occurring. The observed curvature suggests that, in addition to a bimolecular termination, there is a first order termination which becomes significant at low dose rates. Reaction {66} may be such a first order process.

{66} $\cdot CH_2CH_2OH$ + H_2O_2 $\rightarrow$ CH_3CH_2OH + HO_2
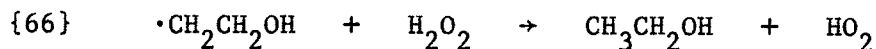
A similar curvature was observed in the dependence of $G(Acetone)$ on $(1/D)^{\frac{1}{2}}$ for the 2-propanol / H_2O_2 chain reaction. In that case the curve can be readily extrapolated to $G^o(Acetone)$ at zero 2-propanol concentration. Such behaviour is implied by equation {65}.

Assuming that at the highest dose rate employed termination is primarily by the bimolecular reaction {64}, it is possible to estimate a lower limit for the rate of the conversion reaction {63}. Using $k_{34}/k_{62} = 8.6$ and assuming that the bimolecular termination reaction has a rate constant $2 k_{64} = 2.0 \times 10^9$ M^{-1} s^{-1}, the value of k_{63} can be calculated from the slope of Fig.4.3. The lower limit for k_{63} was found to be 16 ± 4 M^{-1} s^{-1}. This may be compared with the value 53 ± 15 M^{-1} s^{-1} for the analogous reaction of the β-radical from 2-propanol. The rate constants for the comparable methyl radical reactions, $k_{\cdot CH_3 + (CH_3)_2CHOH}$

$= 3.4 \times 10^3$ M^{-1} s^{-1} and $k_{\cdot CH_3 + CH_3CH_2OH} = 5.9 \times 10^2$ M^{-1} s^{-1},

have been determined by Thomas (44). It is seen that $k_{\cdot CH_3 + (CH_3)_2CHOH}$

is greater than $k_{\cdot CH_3 + CH_3CH_2OH}$ which corresponds to the order

observed with the β-radical reactions, that is, $k_{52} > k_{63}$.

The similarity in the results for the radiation induced chain oxidation of 2-propanol and ethanol confirms that the mechanism is the same in both cases. The results from 2-propanol and ethanol, where two distinctive radical species can be formed from the respective parent alcohol, are now compared with the results from methanol, from which only one radical species can be derived.

0.1 M - 2.0 M Methanol / 10^{-2} M H_2O_2

The oxidation of methanol obeys simple kinetics: The rate of hydrogen peroxide removal is independent of methanol concentration (Table 4.3), dependent on hydrogen peroxide concentration and the square root of the dose rate (Figs.4.7 and 4.8). These results are in direct contrast to the results obtained from 2-propanol and ethanol.

The contrast in the results when methanol is the oxidizable material may be attributed to the fact that only one radical, $\cdot CH_2OH$, may be formed by abstraction from a C-H bond in methanol. In the case of methanol the results conform to the simple mechanistic scheme:

{13} $H_2O \rightsquigarrow e_{aq}^-,\ H,\ OH,\ H_3O^+,\ H_2O_2,\ H_2$

{39} $e_{aq}^- + H_2O_2 \rightarrow OH + OH^-$

{67} $H + CH_3OH \rightarrow H + \cdot CH_2OH$

{68} $OH + CH_3OH \rightarrow H_2O + \cdot CH_2OH$

{69} $H_2O_2 + \cdot CH_2OH \rightarrow HCHO + H_2O + OH$

{70} $2\ \cdot CH_2OH \rightarrow$ Ethylene Glycol, or $HCHO + CH_3OH$
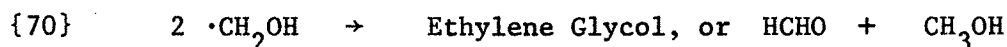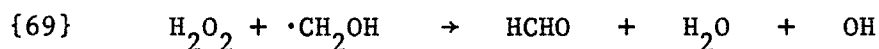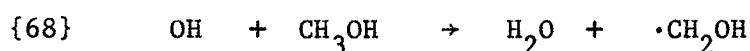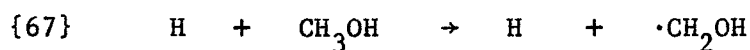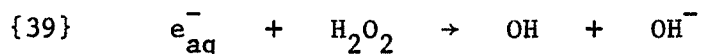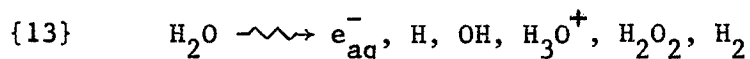
Assuming normal steady-state approximations, the rate of peroxide removal can be expressed in the following form:

$$\{71\} \quad -\frac{d[\,H_2O_2]}{dt} = \left(G_{e^-_{aq}} - G_{H_2O_2}\right)D + k_{69}\left[\frac{\left(G_{e^-_{aq}} + G_H + G_{OH}\right)D}{2\,k_{70}}\right]^{\frac{1}{2}}[H_2O_2]$$

The expression predicts that the rate of peroxide reduction will be independent of methanol concentration and, for moderate to large chain lengths, first order in H_2O_2, which is in excellent agreement with the results. The apparent first order rate constant includes a square root dependence on dose rate which again is in agreement with the experimental results. Apparent first order rate constants are tabulated in Table 4.3. Within experimental error the rate constant for peroxide removal is constant over the range 0.1 M to 2.0 M methanol. Any slight increase in the value of the rate constant with increasing methanol concentration may be due to an increase in the total radical yields. Total radical yields are known to increase with solute concentration (13).

Assuming a value of $2\,k_{70} = 2.4 \times 10^9\ M^{-1}\ s^{-1}$ (52) for the bimolecular termination reaction, a rate constant for the chain propagating reaction may be estimated as $k_{69} = (4.0 \pm 0.4) \times 10^4\ M^{-1}\ s^{-1}$. This is somewhat less than the rate constant found by Seddon and Allen (29) for the propagating reaction in the ethanol--H_2O_2 chain reaction. It may be noted that the rate constant for reduction of ferricyanide by $\cdot CH_2OH$ is slightly less than that for reduction by $CH_3\dot{C}HOH$ (47).

The small yield of ethylene glycol, G(Glycol) $\sim$ 0.5, represents approximately 20% of the termination reactions. In the photolysis of methanol-water solutions (53), the major product of radical combination of $\cdot CH_2OH$ was said to be ethylene glycol.

The principal numerical results are summarized in Table 4.5.

(74)

TABLE 4.5

Principal Numerical Results

Alcohol	% Attack at α-Carbon by OH	$k_{\beta\,+\,Alc.}$ $(M^{-1}\,s^{-1})$	$\left(k_{\alpha\,+\,H_2O_2}\right) \times 10^4$ $(M^{-1}\,s^{-1})$
Methanol	100		4.0 ± 0.4
Ethanol	90	16 ± 4	
2-Propanol	86	53 ± 15	

> 3.0 M Ethanol, Methanol / 10^{-2} M H_2O_2

At high concentrations of ethanol and methanol the respective yields of peroxide reduction decrease to limiting values in the pure solvents (Fig.4.5). This phenomenon has previously been reported for the photoinduced reaction in mixed water-alcohol systems (26) and in the radiation induced oxidation of 2-propanol as discussed in the preceding chapter. In the photochemical system, the variation of peroxide quantum yields with ethanol concentration was attributed to a "photochemical cage" effect and the results with 2-propanol and methanol were said to be similar. The near duplication of the ethanol results shown in Fig.4.5 in the photochemical system suggests that this cannot be a "cage" effect since, in a radiation induced reaction, there is no analogue of the primary solvent cage.

In addition the results with methanol, while similar in that they show a decreasing $G(-H_2O_2)$ yield at high alcohol concentrations, do not display a significant intermediate maximum yield. It has been previously suggested that the increasing yields with increasing 2-propanol, ethanol concentration (for

solute concentrations < 3 M) reflects the increasing rate of reactions {52} and {63}. With methanol, where only one kind of radical may be formed, there is no reaction analogous to {52} and {63} and, correspondingly, no increase in yield with increasing methanol concentration.

With ethanol (or 2-propanol) at sufficiently high alcohol concentration, reaction {63} is no longer the rate controlling step and reaction {35} becomes rate controlling in competition with a second terminating reaction {41}.

{35} H_2O_2 + $CH_3\overset{\cdot}{C}HOH$ → CH_3CHO + H_2O + OH

{41} $2\ CH_3\overset{\cdot}{C}HOH$ → 2,3-Butanediol, or CH_3CHO + CH_3CH_2OH
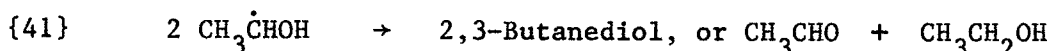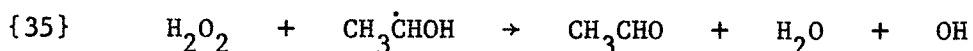
Thus a transition to a situation in which the yield is independent

of alcohol concentration and dependent on $[H_2O_2]$ might be anticipated. The decrease in yields with increasing alcohol concentration could arise from a decrease in the primary radiation chemical yields or, more likely in view of the parallelism with the photochemical results, a decrease in the rate of reaction {35} with decreasing dielectric constant in the high alcohol concentration range. Reaction {35} can be regarded as having a polar transition state. With decreasing dielectric constant at high alcohol concentrations, the activation energy of formation of the polar transition state increases, hence the rate of the propagation reaction and with it the chain length is reduced.

In contrast, methanol, with no mechanism for an initial increase in yield, has a propagation reaction which is initially slower than the corresponding reaction {35} in ethanol. Therefore the rate of the propagating reaction, and with it the chain length, would show a continuous decrease with increasing methanol content as has been observed in the results.

0.51 M Ethanol / < 5 x 10^{-3} M H_2O_2

Below 5 x 10^{-3} M H_2O_2, the chain yields become dependent upon peroxide concentration. This indicates that reaction {35} is slowing down sufficiently to become rate controlling in preference to reaction {63}. Mixed kinetics would probably hold at concentrations slightly less than 5 x 10^{-3} M H_2O_2. But at less than 10^{-3} M H_2O_2 essentially the simple kinetics, predicted by Seddon and Allen (29), would be observed.

4.3 Additional Studies

On completion of work on the chain oxidation of 2-propanol, ethanol and methanol it was decided that a study of the radiation induced oxidation of 2-propanol by hydrogen peroxide in the presence of simple thiols should be undertaken. The 2-propanol-H_2O_2 chain reaction in the presence of simple amines has been previously studied in this laboratory (54). It was observed that increasing the concentration of amine resulted in a decrease in the yield of acetone. The chain formation of acetone was inhibited in the presence of primary, secondary and tertiary amines. Addition of acid almost completely removed any inhibiting effect due to the presence of amine. Mechanisms were proposed to account for the above effects.

It was felt that the presence of thiols might produce a similar inhibitive effect on the chain formation of acetone in the 2-propanol / H_2O_2 system. It is well known that simple SH compounds such as cysteamine ($NH_2CH_2CH_2SH$) can readily transfer hydrogen to a solute free radical X· (55).

{72}   X· + RSH → XH + RS·

It is therefore not unreasonable to assume that in the 2-propanol-H_2O_2 system reaction {73} can occur,

{73} $(CH_3)_2\dot{C}OH$ + RSH → $(CH_3)_2CHOH$ + RS·

in competition with reaction {31}.

{31} $(CH_3)_2\dot{C}OH$ + H_2O_2 → $(CH_3)_2CO$ + OH + H_2O
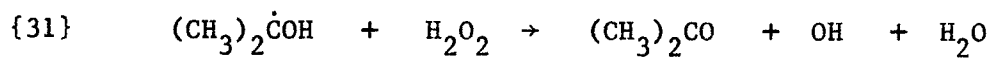
Increasing the thiol concentration should result in a decrease
in G(Acetone). Results of these studies on the oxidation of
2-propanol in the presence of thiols are presented in the following
chapter.

5. INHIBITION STUDIES - RESULTS AND DISCUSSION

Acetone formation yields have been used to monitor the effect of added thiols on the radiation induced oxidation of 2-propanol by hydrogen peroxide. Preliminary studies indicated that there was little radiation induced reaction of hydrogen peroxide with the added thiols, hence no interference was expected from such reactions. All experiments were carried out in degassed solution, since the presence of oxygen also inhibits the chain formation of acetone.

5.1 Results

Acetone formation yields, in the presence of fixed concentrations of 1-propanethiol, at three different concentrations of 2-propanol are tabulated in Table 5.1. The initial concentration of hydrogen peroxide $[H_2O_2]^o = 5.5 \times 10^{-3}$ M.

TABLE 5.1

G(Acetone) at three concentrations of 2-Propanol.

$10^4 \times [1\text{-Propanethiol}]$ (mole 1^{-1})	G(Acetone)		
	$[2\text{-Propanol}] = 0.13$ M	0.52 M	1.05 M
0.0	36.1	51.8	70.1
0.66	29.9	41.6	58.6
1.22	13.7	24.3	34.9
1.87	8.1	16.1	24.1
3.28	3.8	7.7	10.6

For constant concentrations of 1-propanethiol, it is observed
that G(Acetone) increases with 2-propanol concentration in the
range 0.1 M to 1.1 M 2-propanol. That this increase is a linear
relationship is clearly evident in Fig.5.1. The linear relationship
holds for each concentration of 1-propanethiol used. From Fig.5.1
it is seen that the intercept values of G^o(Acetone) at zero 2-
propanol concentration and the slopes of the G(Acetone) v.[2-Propanol]
plots decrease as the concentration of thiol is increased.
Calculated G^o(Acetone) and calculated slopes of G(Acetone) v.
[2-Propanol] at various concentrations of 1-propanethiol are
collected in Table 5.2.

TABLE 5.2

G^o(Acetone) and slope of G(Acetone) v.[2-Propanol]
plots at various concentrations of 1-Propanethiol.
Initial $[H_2O_2]$= 5.5 x 10^{-3} M.

10^4 x [1-Propanethiol] (mole 1^{-1})	G^o(Acetone)	Slope G(Acetone) v.[2-Propanol]
0.0	31.2	36.57
0.66	25.7	31.25
1.22	11.3	22.87
1.87	6.3	17.26
3.28	3.2	7.28

The data in Table 5.1 are presented in a separate form in
Fig.5.2. Fig.5.2 is a graph of G(Acetone) yields plotted against
the concentration of 1-propanethiol. G(Acetone) decreases with
increasing concentration of thiol. The chain production of acetone

Fig.5.1

G(Acetone) v. [2-Propanol] plots at various
thiol concentrations.

10^4 x [1-Propanethiol] : (●) 0.0 M

(○) 0.66 M

(■) 1.22 M

(□) 1.87 M

(▲) 3.28 M

10^4 x [2-Propanethiol] : (△) 3.85 M

(80a)
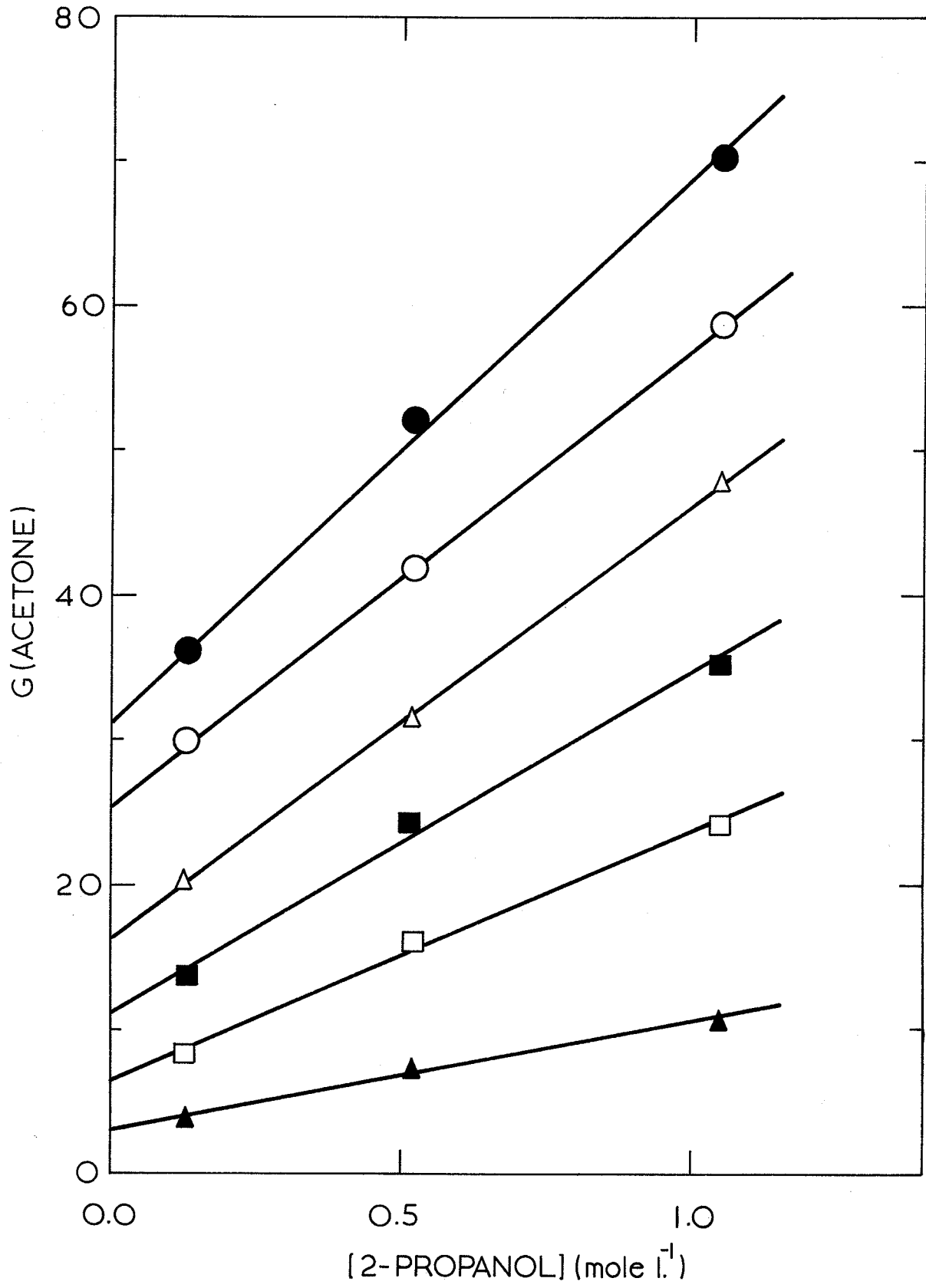
Fig.5.2

Plot of G(Acetone) v. [1-Propanethiol] .
[2-Propanol] : (●) 0.13 M
(○) 0.52 M
(■) 1.05 M

(81a)
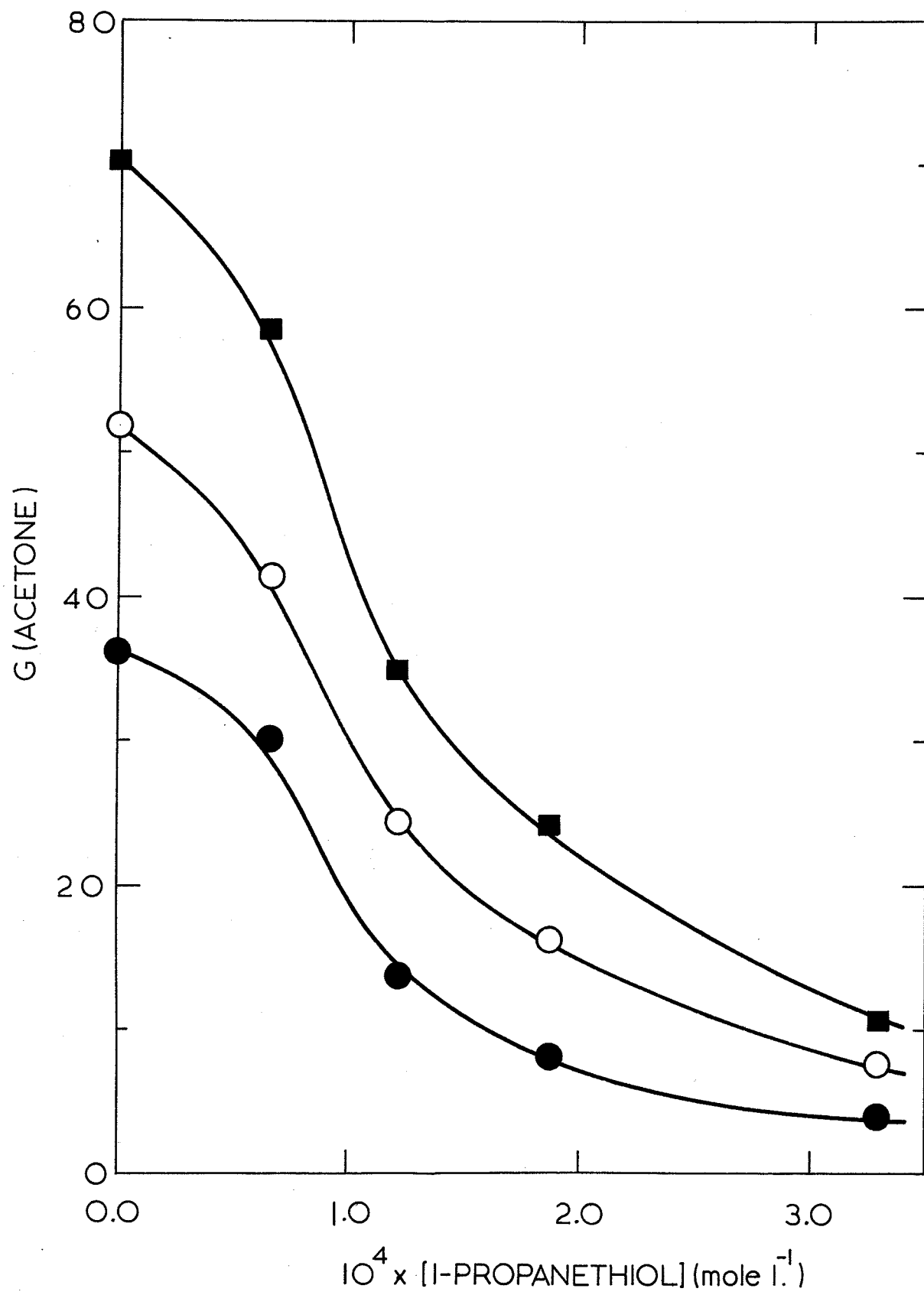
is almost completely inhibited in the presence of 3.28×10^{-4} M
1-propanethiol. Inhibition curves for the three 2-propanol
concentrations (0.13 M, 0.52 M and 1.05 M) studied are shown in
Fig.5.2.

Acetone formation yields have been determined in the
presence of 2-propanethiol. The results are collected in Table 5.3.
G(Acetone) decreases with increasing 2-propanethiol concentration.
The chain reaction is completely inhibited in the presence of
2.2×10^{-3} M 2-propanethiol.

TABLE 5.3

G(Acetone) as function of $[2\text{-Propanethiol}]$.

$[2\text{-Propanol}]$ = 0.52 M. $[H_2O_2]^0$ = 5.5×10^{-3} M.

$10^4 \times [2\text{-Propanethiol}]$ (mole 1^{-1})	G(Acetone)
2.19	48.4
3.85	31.4
5.48	23.4
10.4	15.7
22.3	2.7

For a fixed concentration of 2-propanol (0.52 M) the
relative effectiveness of either 1-propanethiol or 2-propanethiol
as an inhibitor may be gauged from Fig.5.3. G(Acetone) is plotted
against concentration of added thiol. It is seen that 1-propanethiol
is a much more effective inhibitor of the 2-propanol / H_2O_2 chain
reaction than 2-propanethiol.

Fig.5.3

G(Acetone) v. [Thiol] . [2-Propanol] = 0.52 M.

(●) 2-Propanethiol

(O) 1-Propanethiol

(83a)
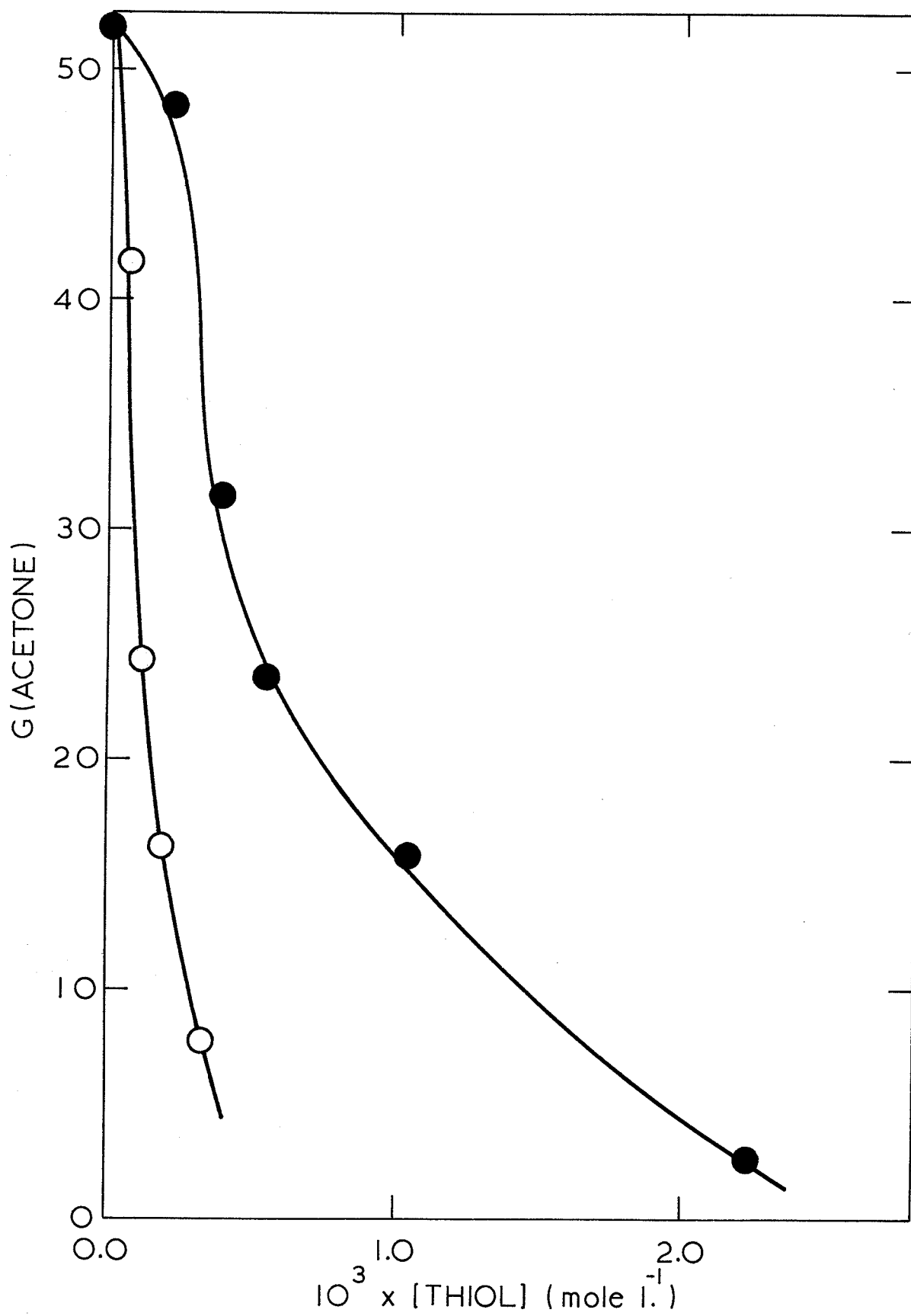
For a fixed concentration of 2-propanethiol, G(Acetone) is found to increase linearly with 2-propanol concentration as shown in Fig.5.1. The results are also tabulated in Table 5.4. Also tabulated is the intercept value at zero alcohol concentration and the slope of the G(Acetone) v. [2-Propanol] plot for that particular concentration of 2-propanethiol used. These results are similar to those observed with 1-propanethiol as the added inhibitor.

TABLE 5.4

G(Acetone) v. [2-Propanol].

$[2\text{-Propanethiol}] = 3.85 \times 10^{-4}$ M. Initial

$[H_2O_2] = 5.5 \times 10^{-3}$ M.

[2-Propanol] (mole l^{-1})	G(Acetone)	G(Acetone) v. [2-Propanol]
0.0	G^o(Acetone) = 16.1	30.05
0.13	20.2	
0.52	31.4	
1.05	47.8	

The effect of increasing the peroxide concentration on the inhibited chain length is shown in Table 5.5. Also, the effects of lowering the dose rate and the pH are also tabulated in Table 5.5. Measurements were carried out at fixed concentrations of alcohol (0.52 M 2-propanol) and added thiol.

Increasing the concentration of hydrogen peroxide restores G(Acetone) to near the normal uninhibited value. A marked dose

TABLE 5.5

Inhibited G(Acetone) yields under various

conditions. [2-Propanol] = 0.52 M.

[Thiol]	Condition	G(Acetone)
1.22 x 10^{-4} M 1-Propanethiol	[H$_2$O$_2$] = 5.5 x 10^{-3} M	24.3
	[H$_2$O$_2$] = 2.75 x 10^{-2} M	43.2
	Dose rate effect: (Attenuation to 26%)	44.3 [a]
	Acid (pH = 1)	27.0 [a]
3.85 x 10^{-4} M 2-Propanethiol	[H$_2$O$_2$] = 5.5 x 10^{-3} M	31.4
	[H$_2$O$_2$] = 2.75 x 10^{-2} M	47.0
	Dose rate effect: (Attenuation to 26%)	42.9 [a]
	Acid (pH = 1)	30.0 [a]

a – Initial [H$_2$O$_2$] = 5.5 x 10^{-3} M.

rate effect on G(Acetone) yields is observed on attenuation of
the normal dose rate to 26%. Little or no effect on G(Acetone)
yields is seen on adjusting the pH of solutions to pH = 1 with
perchloric acid.

5.2 Discussion

It is clearly demonstrated by the preceding results that
the presence of thiols inhibits the chain oxidation of 2-propanol

to acetone. A mechanism is now proposed to account for the inhibition of the formation of acetone:

{13} $H_2O \rightsquigarrow e_{aq}^-$, H, OH, H_3O^+, H_2O_2, H_2

{39} $e_{aq}^- + H_2O_2 \rightarrow OH + OH^-$

{50} $H + (CH_3)_2CHOH \rightarrow H_2 + (CH_3)_2\dot{C}OH$

{51} $H + (CH_3)_2CHOH \rightarrow H_2 + CH_3(\dot{C}H_2)CHOH$

{30} $OH + (CH_3)_2CHOH \rightarrow H_2O + (CH_3)_2\dot{C}OH$

{37} $OH + (CH_3)_2CHOH \rightarrow H_2O + CH_3(\dot{C}H_2)CHOH$

{31} $H_2O_2 + (CH_3)_2\dot{C}OH \rightarrow (CH_3)_2CO + H_2O + OH$

{73} $RSH + (CH_3)_2\dot{C}OH \rightarrow (CH_3)_2CHOH + RS\cdot$

{52} $CH_3(\dot{C}H_2)CHOH + (CH_3)_2CHOH \rightarrow (CH_3)_2CHOH + (CH_3)_2\dot{C}OH$

{74} $CH_3(\dot{C}H_2)CHOH + RSH \rightarrow (CH_3)_2CHOH + RS\cdot$

{53} $2\ CH_3(\dot{C}H_2)CHOH \rightarrow 2,5\text{-Hexanediol, or } (CH_3)_2CO + (CH_3)_2CHOH$
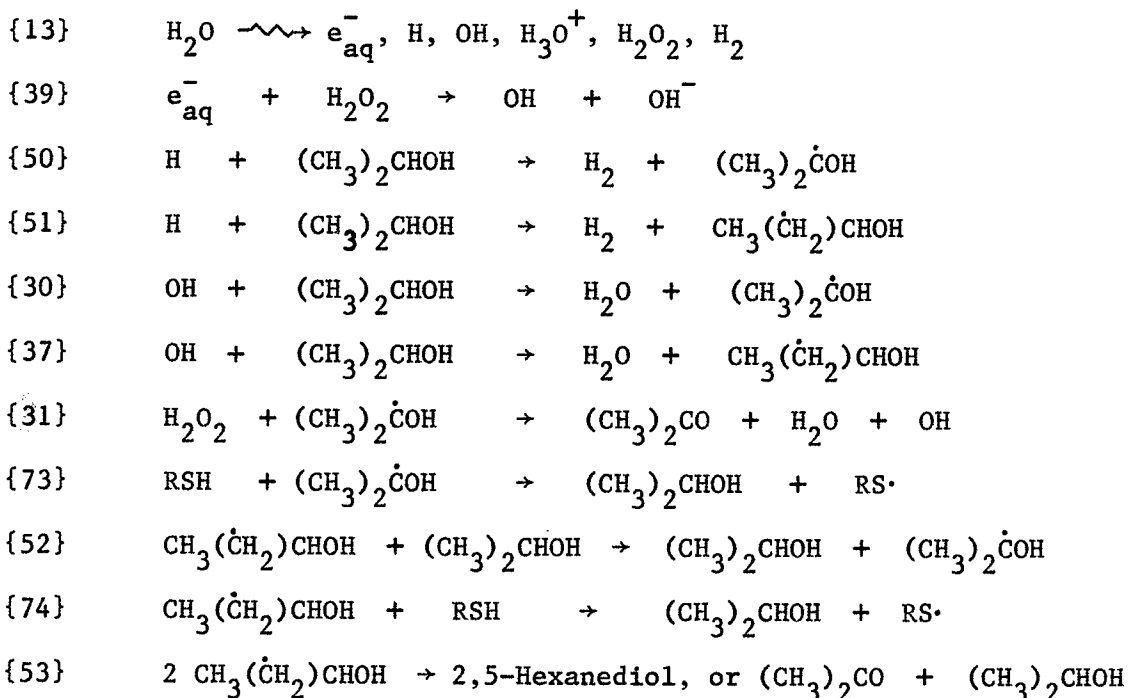
This mechanism is similar to that proposed to account for the inhibition of the chain reaction by amines (54).

Interaction of e_{aq}^- with cysteamine is a fast reaction with a rate constant equal to 2×10^{10} M^{-1} s^{-1} (14). The rate constant of $e_{aq}^- + RSH$ is probably of the same order of magnitude but since $[H_2O_2] > [RSH]$ and $k_{39} = 1.23 \times 10^{10}$ M^{-1} s^{-1} (14), reaction of e_{aq}^- with RSH may be omitted. Also omitted are reactions of H and OH with RSH. Adams et al. (56,57) have found a value of 4.9×10^9 M^{-1} s^{-1} for the rate of reaction OH + Cysteamine, using pulse radiolysis techniques. However, in the radiation induced oxidation of 2-propanol, [2-Propanol] $\gg$ [RSH], hence reaction of OH with RSH can be neglected even though $k_{OH + RSH}$ might have essentially the same value as $k_{OH + Cysteamine}$. No rate constant data are available for OH + RSH and H + RSH to date. It might be assumed that $k_{H + RSH}$ would be slightly greater than k_{50}, but since

[2-Propanol] >> [RSH] , reaction of H with RSH can also be omitted.

Significant features of the mechanism are the inclusion of reactions {73} and {74}.

{73} $(CH_3)_2\dot{C}OH$ + RSH → $(CH_3)_2CHOH$ + RS·

{74} $CH_3(\dot{C}H_2)CHOH$ + RSH → $(CH_3)_2CHOH$ + RS·
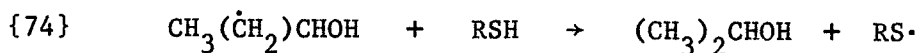
Reaction {73} is suggested by the form of the experimental results: G(Acetone) decreases as the concentration of thiol is increased; the chain reaction is almost completely restored on increasing the concentration of hydrogen peroxide five fold. This evidence suggests that reaction {73} is in competition with reaction {31}.

{31} H_2O_2 + $(CH_3)_2\dot{C}OH$ → $(CH_3)_2CO$ + OH + H_2O
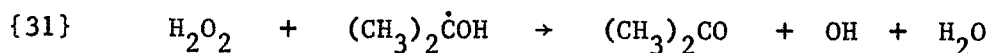
As the concentration of thiol is raised more α-radicals are undergoing the radical repair reaction {73}, rather than reacting with H_2O_2.

The linear **dependence** of acetone yields on 2-propanol concentration suggests that the reaction,

{52} $CH_3(\dot{C}H_2)CHOH$ + $(CH_3)_2CHOH$ → $(CH_3)_2CHOH$ + $(CH_3)_2\dot{C}OH$
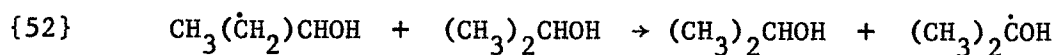
is the rate controlling propagation step in competition with a termination reaction involving β-radicals. The gradual decrease in the slope of G(Acetone) v. [2-Propanol] plots with increasing thiol concentration implies that the β-radical, $CH_3(\dot{C}H_2)CHOH$, is undergoing the radical repair reaction {74}. Reactions {52} and {74} are apparently competitive reactions with {74} being favoured at high thiol concentrations.

Equations {73} and {74} represent first order termination reactions of the chain mechanism. If termination of the chain was solely by first order processes no dose rate effect on the yields would be observed. However, according to the results a significant dose rate effect is observed on attenuation of the

normal dose rate to 26%. Therefore a bimolecular termination reaction in competition with reaction {52} is occurring. The results indicate that reaction {53} is the bimolecular termination process.

{53} $2 \ CH_3(\dot{C}H_2)CHOH \rightarrow 2,5\text{-Hexanediol, or } (CH_3)_2CO \ + \ (CH_3)_2CHOH$
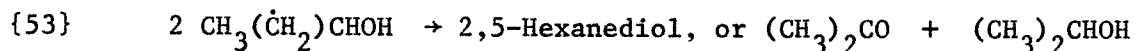
RS· radicals from reactions {73} and {74} probably react by bimolecular combination to form the respective disulphides.

{75} $RS \cdot \ + \ RS \cdot \ \rightarrow \ RS\text{-}SR$
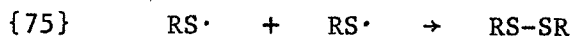
As previously noted, no reaction between H_2O_2 and thiol was

observed on irradiating aqueous solutions of 2-propanethiol

and H_2O_2. This evidence suggests that reaction between RS· and

H_2O_2, the analogue of reaction {31}, is not favoured energetically.

The similarities and the differences between the thiol inhibition and the amine inhibition (54) of the 2-propanol/ H_2O_2 chain reaction are now briefly summarized:

(i) Both thiols and amines effectively inhibit the chain formation of acetone from the 2-propanol / H_2O_2 system. However, the results indicate that the two thiols studied are much more effective inhibitors of the chain reaction than amines. Approximately 0.1 M isopropylamine was needed for almost complete inhibition of G(Acetone) yield compared to 3.28×10^{-4} M 1-propanethiol and 2.2×10^{-3} M 2-propanethiol.

(ii) Isopropylamine, diisopropylamine and triethylamine were equally effective as inhibitors whereas a marked difference was observed between the thiols (Fig.5.3). 1-Propanethiol proved to be a more effective inhibitor than 2-propanethiol.

(iii) The increase in G(Acetone) with 2-propanol concentration was a linear relationship for both thiols used. In the case of an amine inhibited reaction of 2-propanol, the acetone yields increased with 2-propanol concentration. A linear relationship did not hold over the entire alcohol range. The yields were less than would be anticipated from a linear relationship at low

2-propanol concentrations.

(iv) The presence of acid largely eliminated the inhibitive
effect of the added amines. Acid had little or no effect on the
ability of thiols to inhibit the chain reaction (Table 5.5).

Various mechanisms have been proposed to explain the
protection of solutes against the effects of ionizing radiation
by the addition of a second additive. The mechanisms include
(a) prevention, or restriction, of attack on the main solute by
free radical precursors due to competitive scavenging by the
additive; (b) stabilization of a solute free radical by reaction
with the additive molecule or free radical; (c) repair of a solute
free radical by hydrogen transfer from the additive.

Mechanism (c) has been used to explain the protection of
polymers irradiated in the presence of sulphydryl compounds (58).
Scholes and Weiss (59) suggest that in biological systems reduction
of primarily produced radicals R· by another cell constituent YH
(eg. SH compound) may occur by a hydrogen transfer reaction.
Hydrogen transfer reactions have been used to explain the protective
effect of cysteamine on irradiated bacteriophage (60), DNA and
trypsin (61).

Considerable experimental evidence has been obtained for
the free radical repair model. ESR studies (62) have demonstrated
that the presence of cysteamine inhibits free radical formation
in irradiated yeast, probably by a hydrogen transfer reaction.
Cysteamine prevents crosslinking of DNA when irradiated by γ-rays
in the form of a nucleoprotein (63). Pihl et al. (65) have studied
the intermolecular transfer of unpaired spins in frozen aqueous
solution from macromolecules (eg. Sephadex or Thiogel) to
penicillamine (PSH). The transfer is influenced by pH, being
somewhat higher in acid than in neutral and alkaline solutions,
indicating that hydrogen transfer from PSH occurs more readily
than electron transfer from PS$^-$. Since aliphatic thiols have
$pK_{S-H} > 7$, the effect of pH on the extent of transfer might be

expected to appear in the alkaline range.

Pulse radiolysis techniques have been used to follow directly radical repair by cysteamine (55,57,66) and H_2S (67). Rate constants of several repair reactions have been determined (57). Adams (57) has shown that radical repair by cysteamine is favoured in solutions with pH < 8. It was concluded that in radical repair reactions it is the unionized sulphydryl group which is involved in the transfer process. This conclusion is in agreement with the ESR evidence of Pihl et al., (65).

ESR and pulse radiolysis studies have provided sufficient supporting evidence for the hydrogen transfer reactions {73} and {74}.

{73} $(CH_3)_2\overset{\cdot}{C}OH$ +   RSH   → $(CH_3)_2CHOH$ +   RS·

{74} $CH_3(\overset{\cdot}{C}H_2)CHOH$ +   RSH   → $(CH_3)_2CHOH$ +   RS·
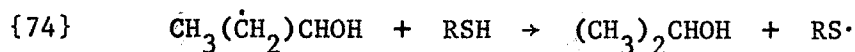
Reactions {73} and {74} are free radical repair reactions indicating that the 2-propanol substrate is protected from radiation damage by mechanism (c). The lack of effect due to the presence of acid (Table 5.5) agrees with earlier observations (57,65) that the unionized sulphydryl group is involved in the repair process. No evidence was found for protection of 2-propanol by mechanisms (a) and (b).

Little information has been gained about the nature of the reaction between any radical R· and SH. Ormerod and Alexander (63) suggest that R· and SH may attain the spacial proximity necessary for hydrogen transfer as a result of molecular movement, or the reaction may depend on the movement of the radical along the molecule by hydrogen atom migration.

In this work it was observed that 1-propanethiol is a more effective inhibitor of the 2-propanol / H_2O_2 chain reaction than 2-propanethiol. This evidence suggests that the interaction of α- and β-radicals with the respective thiols is quite stereospecific, that is, a preferred configuration must be attained before hydrogen

transfer will occur. Hydrogen transfer from 2-propanethiol would require a more highly ordered transition state than hydrogen transfer from 1-propanethiol, resulting in the decreased effectiveness of 2-propanethiol as an inhibitor of the chain reaction. This tends to support the idea that spacial proximity is necessary for hydrogen transfer (63).

No simple yield expression can be derived by steady-state approximations from the inhibition mechanism. Therefore reliable estimates of the rates of reactions {73} and {74} are unobtainable. Adams (57) has determined a rate constant for reaction {76}, $k_{76} = 4.2 \times 10^8 \ M^{-1} \ s^{-1}$.

{76} $NH_2CH_2CH_2SH + (CH_3)_2\dot{C}OH \rightarrow (CH_3)_2CHOH + NH_2CH_2CH_2S\cdot$
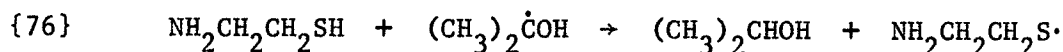
It is possible to speculate that the analogous reaction with 1-propanethiol would have a rate constant of the same order of magnitude ($k_{77} \sim 10^8 \ M^{-1} \ s^{-1}$).

{77} $(CH_3)_2\dot{C}OH + CH_3CH_2CH_2SH \rightarrow (CH_3)_2CHOH + CH_3CH_2CH_2S\cdot$

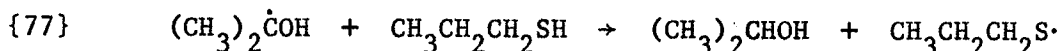Since 2-propanethiol is less effective an inhibitor than 1-propanethiol, reaction {78} may have a rate constant an order of magnitude less than k_{76}.

{78} $(CH_3)_2\dot{C}OH + (CH_3)_2CHSH \rightarrow (CH_3)_2CHOH + (CH_3)_2CHS\cdot$

It is possible that pulse radiolysis may be used to measure directly k_{77} and k_{78}.

For free radical repair of 2-propanol, both thiols are superior to amines, since the hydrogen in the SH group is very labile. It was postulated (54) that amines inhibited the chain reaction by interaction of the 2-propanol radicals with the lone pair of electrons on the nitrogen atom of the amines. It has been noted (65) that the anion S^- is much less effective in radical repair reactions than the unionized SH group. This suggests that amines may be similar to S^- in their ability to repair radicals,

that is, amines repair radicals by an electron transfer process
rather than hydrogen transfer. The lone pair of electrons on the
nitrogen atom is readily available for reaction with a radical
in an electron transfer process accounting for the observation
that primary, secondary and tertiary amines are equally effective
at inhibiting the chain reaction. If amines inhibited the chain
reaction by hydrogen transfer, marked differences would be
observed between the effectiveness of primary, secondary and
tertiary amines as inhibitors.

Supporting evidence for the different repair mechanism
of thiols and amines comes from the acid effect. Acid has little
or no effect on the ability of thiols to transfer hydrogen atoms
and thus no effect on the ability of thiols to inhibit the chain
reaction whereas the ability of amines to inhibit the chain
formation of acetone is largely eliminated by the addition of
acid. The presence of acid has the effect of immobilizing the
lone pair of electrons on the nitrogen atom by forming the
respective protonated amine, for example, $(CH_3)_2CHNH_3^+$. The amines
can no longer partake in electron transfer reactions and hence
lose the ability to inhibit the chain reaction. It may be
concluded that amines protect the 2-propanol by an electron
transfer reaction which may be classified as a modification of
protection mechanism (c).

As described earlier, for a fixed amine concentration, the
G(Acetone) v [2-Propanol] plot deviated from a linear relationship
at low 2-propanol concentrations. It appears that at low alcohol
concentrations the amine may restrict initial attack of H and OH
on 2-propanol by competitive scavenging of these two radicals.
This represents protection of a solute by mechanism (a). The
curvature in the plot implies that amines are protecting the
2-propanol by mechanism (a) and the modified mechanism (c), with
the modified mechanism (c) predominating at concentrations of
2-propanol > 0.3 M. No evidence was found for the protection

mechanisms (a) and (b) in the thiol inhibited chain reaction of 2-propanol / H_2O_2.

5.3 Summary

The presence of simple thiols and amines is found to inhibit the γ-radiation induced chain oxidation of 2-propanol by H_2O_2. Therefore 2-propanol is protected from radiation damage by the presence of thiols and amines, with thiols being more effective protective agents than amines. Thiols protect 2-propanol from radiation damage by H transfer from the unionized sulphydryl group to the alcohol radicals (mechanism c). Amines protect 2-propanol by an electron transfer **reaction** with the alcohol radicals. Hydrogen transfer is a **more** favoured reaction than electron transfer. It is felt that this difference can explain the relative effectiveness of thiols and amines as inhibitors, which may have important implications in the study of radiation damage and protection of biological molecules.

6. SUGGESTIONS FOR FURTHER WORK

There are several worthwhile extensions of the work described in the previous chapters:

1. A detailed study of the photoinduced oxidation of aqueous solutions of 2-propanol by H_2O_2 should be undertaken. The features of the photochemical system should be analogous to the radiation chemical system. Research could be further extended to the study of the photoinduced oxidation of ethanol and methanol by H_2O_2, and the results compared with those found in this work.

Barrett (26) has studied the photoinduced oxidation of ethanol by H_2O_2. The results compare with the radiation chemical study of ethanol. Barrett states that the results from 2-propanol and methanol are similar to those from ethanol whereas this work has shown that the radiation induced oxidation of ethanol and and 2-propanol are similar but both are in marked contrast with the radiation induced oxidation of methanol. Barrett has also extrapolated the plot of $\phi(-H_2O_2)$ v. Mole Percent Ethanol to ϕ_p (primary quantum yield of H_2O_2) at zero alcohol concentration. If the photochemical system is analogous to the radiation chemical system, the plot of $\phi(-H_2O_2)$ v. Mole Percent Ethanol should extrapolate to a large positive intercept at zero alcohol concentration. Therefore, there is obvious disagreement between Barrett's work and the radiation chemical results which can be clarified by the detailed study outlined above.

2. The radiation induced oxidation of isotopically substituted 2-propanol should be studied, to further verify the postulate of non-specific hydrogen abstraction from 2-propanol by H and OH. With $(CD_3)_2CHOH$ as the oxidizeable substrate, the ratio of the rates of hydrogen abstraction by OH from the α- and β-positions, k_α/k_β, should increase from the value of 6.2 found

in this work. This should result in a decrease in the slope of the G(Acetone) v. [Alcohol] plot and also a decrease in the intercept value at zero alcohol concentration.

If $(CH_3)_2CDOH$ were the oxidizable substrate, k_α/k_β would be less than 6.2. The slope of the G(Acetone) v. [Alcohol] plot should increase along with an increase in the intercept value at at zero alcohol concentration. These experiments should provide clear cut evidence for non-specific hydrogen abstraction by H and OH.

3. Initial experiments were carried out in this laboratory in connection with this work on the γ-radiation induced oxidation of ethylene glycol by H_2O_2. It was hoped that the oxidation of ethylene glycol would be analogous to the oxidation of methanol, because one radical species only can be derived from the glycol, $HO\dot{C}HCH_2OH$. It was noted that the rate of peroxide removal was essentially first order, and showed a dependence on dose rate. However, it was observed that acetaldehyde was formed as an unexpected product in chain yields of the order of 8-10. It was suspected that the $HO\dot{C}HCH_2OH$ radical may undergo a rearrangement reaction, with acetaldehyde being formed as an ultimate product of the rearrangement. Such a rearrangement reaction would complicate the overall mechanism. Research should be undertaken to completely characterize the mechanism of the radiation induced oxidation of ethylene glycol.

4. A number of experiments were carried out on the radiation induced oxidation of formic acid and sodium formate by H_2O_2. Formic acid and sodium formate were oxidized to carbon dioxide in chain yields, the extent of the reaction being monitored by measuring the peroxide removal. The chain reaction was studied over a wide range of pH and the results were found to be rather irreproducible. The pH dependence of $G(-H_2O_2)$ yields showed rough agreement with the results of Husain and Hart (34). Their results also showed a similar degree of irreproducibility. If further

experiments are to be carried out on the formic acid, sodium formate / H_2O_2 systems it would be advisable to carefully control 1) the amount of impurities and 2) the pH of each solution, to obtain reliable results.

5. The radiation induced oxidation by hydrogen peroxide of a wide variety of organic substrates remains to be done, for example, higher alcohols, diols, aldehydes and acids. In addition it is possible that this work could be extended to aromatic systems.

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