THE RADIATION-INDUCED OXIDATION OF SIMPLE HYDROCARBONS IN AQUEOUS SOLUTIONS

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ABSTRACT

The γ-radiolysis of aqueous solutions of ethane (1.0×10^{-3} M) oxygen (7.0×10^{-4} M) resulted in the formation of the products, acetaldehyde with G = 1.6; ethyl hydroperoxide G = 0.9; and hydrogen peroxide G = 2.0 at pH 5.5. At pH 1.2, the yields were acetaldehyde G = 2.4; ethanol G = 0.4; and hydrogen peroxide G = 3.7. G (organic products) = G_{OH} in the pH range investigated indicated the absence of chain reactions in this system. The formation of the observed products can be accounted for by following overall reactions:

$$CH_3.CH_3 + OH \dashrightarrow CH_3.CH_2. \qquad (1)$$

$$CH_3.CH_2. + O_2 \dashrightarrow CH_3.CH_2.OO \qquad (2)$$

$$2\ CH_3.CH_2.OO \dashrightarrow CH_3.CHO + CH_3.CH_2OH + O_2 \qquad (3)$$

$$2\ CH_3.CH_2.OO \dashrightarrow 2\ CH_3.CHO + H_2O_2 \qquad (4)$$

$$CH_3.CH_2.OO + O_2^- \xrightarrow{H_2O} CH_3.CH_2OOH + O_2 \qquad (5)$$

The evidence for reaction (5) was obtained by irradiating in the presence of nitrous oxide and also from the photolysis of ethane-oxygen aqueous solutions where O_2^- ions are not formed.

In γ-irradiated methane-oxygen aqueous solutions, saturated with the gases at atmospheric pressure, secondary reactions involving the products commenced at an early stage in the radiolysis; this was due to the low reactivity of methane towards hydroxyl radicals. When the concentration of the gases was increased by a factor of about 20 $[CH_4] = 2.0 \times 10^{-2}$ M, $[O_2] = 3.5 \times 10^{-3}$ M, the products and yields were , at pH 5.5. G (HCHO) = 0.55; G (CH_3OOH) = 1.65; and G (H_2O_2) = 2.1 and at pH 2.0, G (HCHO) = 1.2; G (CH_3OH) = 1.3; G (HCOOH) = 0.98; and G (H_2O_2) = 3.5. The reduction in the yield of methyl hydroperoxide in the presence of nitrous oxide and its absence as a product in the photolysis at pH 5.5 and 2.0, and radiolysis at pH 2.0, indicated that this product was formed via processes similar to (5). The formation of the remaining products of methane

oxidation in aqueous solutions can be explained by following overall stoichiometries:

$$2\ CH_3.OO \longrightarrow HCHO + CH_3OH + O_2 \qquad (6)$$

$$2\ CH_3.OO \longrightarrow 2\ HCHO + H_2O_2 \qquad (7)$$

$$CH_3.OO + O_2 \longrightarrow HCOOH + HO_2 \qquad (8)$$

The photolysis of hydrogen peroxide solutions in the presence of ethylene-oxygen mixtures was undertaken to clarify some aspects of the γ-radiolysis of this system investigated previously.

The average product yields per molecule of hydrogen peroxide decomposed were at pH 5.5, HCHO = 1.03; $HO.CH_2.CHO$ = 0.95; HCOOH = 0.5; and $HO.CH_2.CH_2OOH$ = 0.28 and at pH 2.0 the yields were, 1.08, 1.1, 0.17 and 0.16 respectively. It was also shown that at pH 5.5 and 2.0 photolysis, 0.3 and 0.42 molecules of hydrogen peroxide respectively were reformed per molecule of hydrogen peroxide decomposed. Furthermore, it was demonstrated that under the conditions where H atoms and electrons were absent, no acetaldehyde was formed.

Some experiments were carried out in which aqueous solutions of ethylene-oxygen were irradiated with U-V light at 1850 A°. Under these conditions, acetaldehyde was a major product showing that hydrogen atoms were essential at some stage in the formation of this product.

The formation of the products in ethylene-oxygen system can be explained by reasonable reactions of hydroxy ethyl peroxy radicals and there appears to be no evidence for the participation of vinyl radicals formed by hydrogen abstraction from ethylene.

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CHAPTER 1

INTRODUCTION

Ever since the discovery of chemical effects of ionizing radiations (Debierne 1914) attempts have been made to develop a satisfactory model to explain the observed facts and to predict the way in which ionizing radiations can affect systems containing water. In this connection both chemical and physical techniques have been extensively employed. It is interesting to note that much of the incentive for the development of such a model has a strong biochemical and biophysical background.

It is well known that ionizing radiations introduce fast electrons into irradiated water. The electromagnetic fields of these fast electrons interact with electrons of water molecules and give rise to further ionization. The electrons produced in these ionizations may be sufficiently energetic to give branches of further ionizations. Irradiated water originally contains excited water molecules, ionized water molecules and electrons. The role of excited water molecules produced by direct excitations or by capture of electrons by ionized water molecules is by no means clear and it is generally believed that the apparent unimportance of excitation may in part be due to close geometrical distribution of H and OH radicals in the solvent cage. The decomposition of water by ionizing radiations on this model can be represented as follows:

$$H_2O \dashrightarrow H + e_{aq}^- + H^+ + OH + H_2 + H_2O_2 \quad (1)$$

Hydrogen and hydrogen peroxide are produced in the spurs where there is a high concentration of radicals and are called as molecular products of the radiolysis of water. The steady state concentration of these radicals has been calculated on the assumption that they are uniformly distributed in the irradiated water (Fricke 1955), and is of the order of 10^{-6} M. However, the radicals are not uniformly distributed and their concentration outside the spurs is likely to be

[illegible]

smaller than that within.

Detection of Reactive Species produced in Irradiated Water.

Weiss suggested that chemical effects of ionizing radiations in water and aqueous solutions could be explained in terms of free radicals such as hydrogen atoms and hydroxyl radicals. (Weiss 1944). The actual evidence as to the existence of these radicals and related species has come only in the recent years.

Solvated electron (e_{aq}^-).

The existence of solvated electrons (also called hydrated electrons) in irradiated water was first suspected when rates of reactions of the reducing radical, thought to be a hydrogen atom, were investigated. Barr and Allen showed that the hydrogen atom (which they called H') produced by oxidation of dissolved hydrogen by OH radicals, react faster with oxygen than with hydrogen peroxide whereas the reducing species (which they called H) produced in the irradiated water not containing dissolved hydrogen, reacts with oxygen and hydrogen peroxide at a comparable rate (Barr and Allen 1959).

$$OH + H_2 \longrightarrow H_2O + H' \qquad (2)$$

$$H' + O_2 \longrightarrow HO_2 \qquad (3)$$

$$H' + H_2O_2 \longrightarrow OH + H_2O \qquad (4)$$

$$H + O_2 \longrightarrow O_2^- \qquad (5)$$

$$H + H_2O_2 \longrightarrow OH + OH^- \qquad (6)$$

Anderson and Hart found that the reducing species reacts with hydrogen peroxide five times faster in neutral solutions than in acidic solutions (Anderson and Hart 1961). This again indicated the different nature of the reducing radical at acid and neutral pH. Czapski and coworkers introduced hydrogen atoms from a silent electric discharge into solution and found that the rate constants derived in this way were similar to those of reducing species in acidic solutions (Czapski 1961). From this observation it was argued that if hydrogen atoms are reducing species in acidic solutions then electrons must be the reducing species in neutral solutions. This suggestion was strengthend by studies on the radiolysis of aqueous solutions of chloroacetic acid (Hayon 1961). In acidic solutions hydrogen was the major product but in neutral solutions this was largely replaced by chloride ions:

$$\text{H} + \text{Cl.CH}_2\text{COOH} \dashrightarrow \text{Cl.}\underset{\bullet}{\text{C}}\text{H.COOH} + \text{H}_2 \qquad (7)$$

$$\text{e aq}^- + \text{Cl.CH}_2\text{COOH} \dashrightarrow \bullet\text{CH}_2\text{.COOH} + \text{Cl}^- \qquad (8)$$

Perhaps the most valuable contribution in this direction came by the study of effect of ionic strength on the rate constants of the reducing species in neutral solutions (Czapski and Schwarz 1962). It was shown that the charge on the reducing species is minus one unit.

More recently physical methods of identification of reactive species produced in irradiated water have come into prominence. These methods are based on light absorption or electron spin resonance spectrum of the radicals and are fairly specific. The principle advantage of these methods over purely chemical methods being that species under investigation can be physically observed. Further large number of data can be obtained in relatively short time and if other radicals and solutes do not interfere strongly, the results can be easily interpreted.

Pulse radiolysis of deaerated water showed the presence of a broad absorption band near 7000 Å (Boag and Hart 1962 & 1963). This absorption spectrum is similar to the absorption spectrum of an alkali metal solution in liquid ammonia and on that basis the presence of electron in irradiated water was inferred. Gordon and Hart have given a spectrophotometric method for the detection of solvated electrons in γ-irradiated millimolar sodium hydroxide solution and also calculated the concentration of electrons, $e_{aq}^{-} = 1.4 \times 10^{-8}$ M (Gordon and Hart 1965).

Hydrogen atom

Although it has been clearly shown that in neutral solutions solvated electrons are the predominant reducing species (Baxendale 1962) there is strong evidence for the existence of hydrogen atom as well. Allen and Scholes in their work on the radiolysis of aqueous solutions of propanol showed that there is a residual yield of reducing species which cannot be scavenged by electron scavengers at pH 5.5. This observation prompted them to suggest that this residual yield could be due to hydrogen atoms (Allan 1960). Lifshitz in his work on the radiolysis of light and heavy water mixtures containing formate ions showed that the composition of molecular hydrogen was different from the hydrogen formed by abstraction: (Lifshitz 1962).

$$HCOO^{-} + H \longrightarrow H_2 + COO \qquad (9)$$

It was also suggested that reaction (9) contributes hydrogen yield corresponding to $G_{(H)} = 0.6$. Hayon and Dainton and Watt have suggested that the so called hydrogen atom in the neutral solutions is really an excited water molecule and it is interconvertible to an electron or hydrogen atom according to the medium (Hayon 1964) and (Dainton 1963).

$$H_2O^{*} \longrightarrow H + OH \qquad (10)$$

$$H_2O^{*} \xrightarrow{O_2} H_2O^{+} + O_2^{-} \qquad (11)$$

However, an excited water molecule species has not been identified so far. Comparison of the kinetics of the doubtful hydrogen atoms (in neutral solutions) with those of known hydrogen atoms (acidic solutions and solutions in which hydrogen atoms were introduced from a silent electric discharge) by Scholes and Simic and by Czapski, Rabani and Stein supported the belief that hydrogen atoms were formed in small yields in neutral solutions (Scholes 1964) and (Czapski 1962). Anbar and Myerstein however have doubted this contention because similar kinetic studies of the so called hydrogen atoms in neutral solutions gave different values of rate constants than that obtained by hydrogen atoms in acidic solutions (Anbar 1964). They have put forward the idea that the so called residual hydrogen atom in neutral solutions or its precursors are excited water molecules. Navon and Stein have made an extensive study of the kinetics of residual hydrogen atoms and known hydrogen atoms and from seven reasonably well established rate constants have again stressed that unless further information is available, the residual reducing radical should be regarded as hydrogen atom (Navon 1965).

Reactions of solvated electrons and hydrogen atoms.

Electrons and hydrogen atoms are reducing radicals formed in irradiated water. Their reactions with wide variety of solutes have been investigated and the conclusions drawn from such studies are of immense help in interpreting chemical effects of ionizing radiations in water and aqueous solutions. Some of the more important cases are reported below.

Reaction	Rate constant k = M^{-1} Sec^{-1} x 10^{-9}
$\bar{e}$ aq + $H^+ \dashrightarrow H$	21.6
+ $CO_2 \dashrightarrow CO_2^-$	7.67
+ $H_2O_2 \dashrightarrow OH + OH^-$	12.3
+ $O_2 \dashrightarrow O_2^-$	19.0
+ $N_2O \dashrightarrow N_2 \cdot OH + OH^-$	5.6
+ $NO_3^- \dashrightarrow NO_3^{-2}$ (?)	10.0
+ $CH_3.CO.CH_3 \dashrightarrow (CH_3CO.CH_3)^-$	5.9

$H + H \longrightarrow H_2$	13.0
$+ OH \longrightarrow H_2O$	10.0
$+ O_2 \longrightarrow HO_2$	19.0
$+ HO_2 \longrightarrow H_2O_2$	20.0
$+ H_2O_2 \longrightarrow OH + H_2O$	0.04
$+ C_6H_6 \longrightarrow C_6H_5^{\bullet} + H_2$	0.07
$+ C_2H_5OH \longrightarrow C_2H_4OH + H_2$	0.015
$+ HCHO \longrightarrow H_2 + {\bullet}CHO$	0.005
$+ HCOOH \longrightarrow H_2 + {\bullet}COOH$	0.001
$+ CH_3OH \longrightarrow {\bullet}CH_2OH + H_2$	0.0016

These rate constants were summarized by Anbar and Neta (1965).

Hydroxyl radical

The hydroxyl radical is the principle oxidising species formed in the radiolysis of water. Like other radicals its existence in the irradiated water has been postulated for some time but actual identification of the species was hampered by such factors as reliable source of its production and its low absorption of light. Almost all the earlier information came from Fenton's reagent studies but there is now some doubt that this reagent produces OH radicals. Hochanadel compared the reactivites of hydroxyl radicals produced in the photolysis of hydrogen peroxide solution and in the irradiated water (Hochanadel 1962). Hydrogen and hydrogen peroxide were used as hydroxyl radical scavengers and it was shown that $k (OH + H_2) / k (OH + H_2O_2)$ was same for hydroxyl radicals produced in both the radiolysis and photolysis. It has been shown that the oxidising species is uncharged and that the rate constant for the reaction (12) is unaffected by ionic strength (Hummel 1962)

$$OH + Br^- \longrightarrow Br + OH^- \qquad (12)$$

Adams and Boag have described a novel technique to study the kinetics of hydroxyl radicals; they react with carbonate ions to give a species which absorbs at 6000 Å and disappears in a bimolecular fashion with a lifetime greater than 10^{-5} second. solutes which react with hydroxyl radicals are found to dedrease this absorption and by following the optical density as a function of solute concentration,relative rate constants for several solutes have been determined (Adams and Boag 1964). More recently rate of reaction of hydroxyl radicals with iodide ions was investigated by pulse radiolysis technique (Thomas 1965). At relatively low iodide ion concentration a transient absorption was observed at 3000 Å and it was attributed to hydroxyl radicals as it was found that addition of electron scavengers as nitrous oxide doubled this absorption.

$$N_2O + e_{aq}^{-} \longrightarrow N_2 + OH + OH^{-} \qquad (13)$$

OH is a strongly oxidising radical and reacts with both organic and inorganic solutes. The most important reaction with organic molecules is dehydrogenation and chemical effects due to hydroxyl radicals can be enhanced by addition of hydrogen peroxide and nitrous oxide:

$$e_{aq}^{-} + H_2O_2 \longrightarrow OH + OH^{-} \qquad (14)$$

The reverse process, an increase in the number of hydrogen atoms at the expense of hydroxyl radicals, is accomplished by the presence of hydrogen or carbon monoxide,

$$OH + H_2 \longrightarrow H + H_2O \qquad (15)$$

$$OH + CO \longrightarrow H + CO_2 \qquad (16)$$

Some of the important reactions of hydroxyl radicals and rate constants are summarised below,

Reaction	$k = M^{-1} \; Sec^{-1} \; x \; 10^{-9}$
$OH + OH \longrightarrow H_2O_2$	6.0
$+ Cl^- \longrightarrow Cl + OH^-$	0.02
$+ Fe^{+2} \longrightarrow Fe^{+3} + OH^-$	0.32
$+ H_2 \longrightarrow H + H_2O$	0.045
$+ HO_2 \longrightarrow H_2O + O_2$	15.0
$+ H_2O_2 \longrightarrow H_2O + HO_2$	0.045
$+ HSO_4^- \longrightarrow HSO_4 + OH^-$	0.02
$+ CH_3.CHO \longrightarrow \bullet CH_2.CHO + H_2O$	0.7
$+ CH_3.CH_2OH \longrightarrow CH_3.\underset{\bullet}{C}HOH + H_2O$	3.0
$+ HCHO \longrightarrow \bullet CHO + H_2O$	2.0
$+ HCOOH \longrightarrow H_2O + \bullet COOH$	0.25
$+ CH_3OH \longrightarrow \bullet CH_2OH + H_2O$	1.8

The rate constants listed above were summarised by Anbar and Neta (1965).

Molecular products.

In the early days of radiation chemistry it was generally believed that molecular products of radiolysis of water vis hydrogen and hydrogen peroxide, originate in the spurs by radical recombination processes,

$$H + H \longrightarrow H_2 \qquad (17)$$

$$OH + OH \longrightarrow H_2O_2 \qquad (18)$$

Hayon and Weiss suggested that solvated electrons may be the precursors of molecular hydrogen and proposed the following reaction for its formation, (Hayon 1958)

$$e\,aq^- + e\,aq^- \longrightarrow H_2 + 2\,OH^- \qquad (19)$$

Dorfman and Taub have confirmed the existence of reaction (19) and measured a rate constant for it (Dorfman 1963). More recently studies have been conducted on the scavenging of molecular hydrogen by high solute concentrations and from the comparison of scavenging efficiencies of various solutes, the presence of two precursors of molecular hydrogen was indicated. Analysis of kinetic data showed them to be solvated electrons and hydrogen atoms, undergoing reactions (19) and (20)

$$e\,aq^- + H \longrightarrow H_2 + OH^- \qquad (20)$$

Reaction (17) was also shown to contribute a small amount to the observed molecular hydrogen yield (Hayon 1965).

Bayakov studied the effect of hydroxyl radical scavengers on $G_{(H_2O_2)}$ and concluded that reaction (18) accounts for the observed yield (Bayakov 1964). However, the relative effectiveness of various scavengers in lowering $\underset{OH}{G_{(H_2O_2)}}$ in neutral solutions is not in good accord with their known reactivities (Hummel and Allen 1962) and (Hughes and Willis 1963).

Radical and molecular yields

Irradiation of water produces reducing and oxidizing radicals and their yields are related by the equation of material balance as follows,

$$G_{(e\,aq^- + H)} + 2\,G_{(H_2)} = G_{(OH)} + 2\,G_{(H_2O_2)}$$
$$= G_{(-H_2O)}$$

Following G values of these species were found for neutral water (Balkas 1966).

$G_{(e\ aq^-)} = 2.30$ $\qquad G_{(OH)} = 2.2$

$G_{(H)} = 0.55$ $\qquad G_{(H_2O_2)} = 0.74$

$G_{(H_2)} = 0.48$

Thus in neutral water $G_{(-H_2O)} = 3.7$

It is generally agreed that whereas yields of molecular products are substantially independent of pH, $G_{(-H_2O)}$, $G_{(OH)}$ and $G_{(e\ aq^- + H)}$ each decrease by about 0.9 units as the pH is increased from 1.4 to 2.2. Thereafter, yields of the radicals as listed for neutral water remain materially the same upto about pH 12. It has not been possible to determine accurately the yields of radicals at pH values in excess of 12.0 as the results of various workers are conflicting (Dainton 1962) , (Haissinsky 1962) , (Haissinsky 1963) and (Linnenbom 1963). Dainton has pointed out some of the limitations of using alkaline solutions of heavy metal ions in studies of this kind and has suggested the use of oxygen and carbon monoxide as solutes for high pH aqueous solution radiation chemistry. These solutes are thought to be simple and not affected by strong alkali solutions (Balkas 1966).

Hayon subscribes to the generally accepted view that yields of radicals increase above pH 12.0 and he has explained this increase in terms of the reactions of OH^- with excited water molecules,(Hayon 1965)

$$OH^- + OH(spurs) \dashrightarrow O^- + H_2O \qquad (21)$$

Reaction (21) thus prevents the back formation of water . Another contribution to the existing literature comes from the work of (Buxton and Dainton 1965). They investigated the radiolysis of potassium iodide aqueous solutions containing nitrous oxide at pH range 0.1 to 14.0 , The results were interpreted in terms of $G_{(e\ aq^-)} = 2.3$ and $G_{(H)} = 0.6$ over the entire pH range. Further excited water molecules are also formed which can react with the solutes as follows,

$$N_2O + H_2O^* \longrightarrow N_2 + 2\ OH \qquad (22)$$

$$OH^- + H_2O^* \longrightarrow e\ aq^- + OH \qquad (23)$$

$$H^+ + H_2O^* \longrightarrow H_2^+ + OH \qquad (24)$$

In other words the available yield of radicals as listed for neutral water, can increase in the presence of adequate concentration of oxygen, nitrous oxide, protons from acids and OH^- from alkalies.

1.1. Rôle of Oxygen and Hydrogen Ion concentration in the Radiation Chemistry of Aqueous Solutions.

Rôle of oxygen.

Dissolved oxygen reacts with the primary reactive species, hydrogen atoms and electrons as well as with the secondary species produced by the reactions of radicals with the solute,

$$H + O_2 \longrightarrow HO_2 \qquad (25)$$

$$e\ aq^- + O_2 \longrightarrow O_2^- \qquad (26)$$

$$OH + R\text{-}H\ (\text{solute}) \longrightarrow H_2O + R\cdot \qquad (27)$$

$$R\cdot + O_2 \longrightarrow RO_2 \qquad (28)$$

Reactions (25) and (26) are very fast and in the absence of high solute concentrations, predominate over a wide range of pH.

The species HO_2 and O_2^- have been identified by their respective absorption spectra (Baxendale 1962) and (Czapski and Dorfman 1964) HO_2 radicals behave both as oxidizing and reducing agents and their reactions with both inorganic and organic solutes have been extensively studied. The role of HO_2 is pertinent to this work and will be discussed in that context.

In the absence of oxygen hydrogen atoms along with hydroxyl radicals can abstract hydrogen from an organic compound,

$$H \quad + \quad R\text{-}H \dashrightarrow H_2 \quad + \quad R\cdot \qquad (29)$$

When dissolved oxygen is also present, reaction (29) is largely replaced by reaction (25). HO_2 radicals formed in this way usually do not abstract hydrogen from organic solutes as reaction (30) is about 10 K Cal more endothermic than reaction (29)

$$HO_2 \quad + \quad R\text{-}H \dashrightarrow H_2O_2 \quad + \quad R\cdot \qquad (30)$$

HO_2 radicals, under these conditions, dismutate in a bimolecular manner to give hydrogen peroxide,

$$HO_2 \quad + \quad HO_2 \dashrightarrow H_2O_2 \quad + \quad O_2 \qquad (31)$$

The rate constant for reaction (31) has been measured by various workers and is of the order of $10^6\ M^{-1}\ Sec^{-1}$ (Schmidt 1960), (Bielski 1962) and (Baxendale 1962). Hydrogen peroxide being stable appears as one of the products of radiolysis of such systems. The main role of oxygen is thus to reduce G (- R-H) by scavenging hydrogen atoms. Secondly, oxygen inhibits the further reaction of R. radicals produced via reaction (27) and (29).

$$R\cdot \quad + \quad R\cdot \dashrightarrow R\text{-}R \qquad (32)$$

In the presence of oxygen, reaction (28) being very fast, predominates over reaction (32). The formation of organic peroxy radicals has been observed in the pulse radiolysis studies on aerated cyclohexane aqueous solutions (McCarthy and McLachlan 1961).

The pH effects.

The effects of pH on the yields of radicals and molecular products in water radiolysis has been discussed previously. A collection of important pH dependent reactions is given below.

Conversion of solvated electrons to hydrogen atoms in acidic solutions,

$$e_{aq}^{-} + H^{+} \longrightarrow H \qquad (33)$$

Possibly followed by slow association of hydrogen atoms with hydrogen ions,

$$H + H^{+} \longrightarrow H_2^{+} \qquad (34)$$

Dissociation of hydroxyl radicals in alkaline solutions,

$$OH \longrightarrow H^{+} + O^{-} \qquad (35)$$

Conversion of hydrogen atoms to solvated electrons in alkaline solutions,

$$H + OH^{-} \longrightarrow e_{aq}^{-} \qquad (36)$$

Dissociation of perhydroxyl radicals in neutral or alkaline solutions,

$$HO_2 \longrightarrow H^{+} + O_2^{-} \qquad (37)$$

pK values for ionization of hydroxyl radicals between 10 and 11.0 have been reported by Hart and others (Hart, 1953) and (Koulkes - Pujo 1957) and any significant effect due to O^{-} ion would be observed in the pH range 10 - 11 . Adams and coworkers claim to have identified O^{-} which absorbs at 2600 A° (Adams 1965). By the study of a large number of inorganic solutes it has been found that as far as oxidation reduction reactions are concerned, the behaviour of OH radicals is not very different from that of O^{-}.

To explain the oxidizing behaviour of hydrogen atoms in acidic solutions, the existence of H_2^+ was suggested by Rigg, Stein and Weiss (Rigg 1952). The presence of this species has also been considered necessary to interpret the results obtained by radiolysis of aqueous solutions of potassium iodide and nitrous oxide (Czapski and others 1959) and (Dainton and Peterson 1962). A recent work, on the effect of pulse intensities on the kinetics of reducing radicals, appears to support the existence of such a species (Thomas 1965). It was shown that at relatively low pulse intensities the molecular hydrogen arises mainly from the recombination of hydrogen atoms and at high pulse intensities, molecular hydrogen arises from the recombination of H_2^+ species. The latter reaction was found to be much slower than hydrogen atom recombination.

Czapski and Bielski have reported the pK value of $HO_2 = 4.45$. (Czapski 1963). This value was essentially confirmed by a more recent work (Rabani, Mulac and Matheson 1965). On this basis the pH effects in the radiolysis of oxygen containing solutions, have been explained in terms of O_2^- ion. Reactions of O_2^- ion are not very well understood but it is generally believed that it is a stronger reducing agent than HO_2. Johnson and Weiss pointed out that charge transfer from O_2^- to other species present in irradiated water can occur.(Johnson and Weiss 1955).

Evidence has also been obtained for the conversion of hydrogen atoms to solvated electrons(Allan, Robinson and Scholes 1962). Alkaline aqueous solutions of organic alcohols were irradiated in the presence of acetone, which scavenges solvated electrons without producing molecular hydrogen. The yield of hydrogen was shown to be decreasing with increasing OH^- ion concentration. This observation was explained by the effect of OH^- concentration on the competition of reactions (29) and (36)

$$H + OH^- \longrightarrow e\ aq^- \qquad (36)$$

$$H + R\text{-}H \longrightarrow H_2 + R\cdot \qquad (29)$$

The preceding discussion has shown that pH may markedly influence the reactions occuring in irradiated water and perhaps to an even greater extent in the irradiated aqueous solutions. In some solutions pH changes will alter the structure of the solute, but in all solutions pH changes may alter the nature and reactivity of the primary radicals and consequently of the products which are derived from them. Some of these changes have been mentioned in the discussion on the nature of reducing radicals in irradiated water.

1.2. Reactivities of Radicals in Aqueous Solutions

The study of the kinetics of free radicals and related species has been the main source of information as regards the identification of primary products of radiation-induced water decomposition. The reactivities of free radicals with scavenging solutes have been studied largely by competition kinetics.

$$\text{R (radical)} + \text{X} \longrightarrow (\text{product})_x$$

$$\text{R (radical)} + \text{Y} \longrightarrow (\text{product})_y$$

If the yields of products x and y can be determined then,

$$\frac{G\ (x)}{G\ (y)} = \frac{k\ x\ (X)\ (R)}{k\ x\ (Y)\ (R)}$$

The radical concentration (R) cancels out and the rate constant ratio $k\ (x)\ /\ k\ (y)$ can be determined by following the variation in the ratios of yield $G\ (x)\ /\ G\ (y)$ with their respective concentrations.

In most cases however, only one yield say G (x) is measured and the other is assumed as G (R) - G (x). This method has been used in the present work to evaluate rate constant for the reaction between hydroxyl radicals and ethane in aqueous solutions

$$OH + CH_3.CH_3 \dashrightarrow CH_3.\dot{C}H_2 + H_2O \qquad (38)$$

A large number of rate constant ratios have been evaluated by the study of competition kinetics and it is only necessary to know the absolute rate constant for one of these reactions to determine the absolute rate constants for all other reactions. Absolute rate constants have been determined from the radical lifetimes given by the expression $t^{-1} = k\ (x)$, where x represents reactive solutes including radicals themselves and k is the absolute rate constant. An example of this type of study is provided by the work of Schwarz on the radiolysis of pure water and ferrous sulphate solutions (Schwarz 1962 and 1964).

Direct methods of determining absolute rate constants have been developed for certain systems. A short pulse of high intensity radiation (usually electrons from an accelerator) is given to the system and the change in the concentration of the reactant or of the product is studied as a function of time. The characteristics of such short pulses of radiations are that the time of irradiation is comparable to the radical lifetime and reactive species are produced in high concentrations along the path of the pulse. Synchronised with this short pulse is the operation of a detection device based on light absorption by the transient species or on electron spin resonance. The limitation in applying this technique is that the solute itself or in reduced form should not absorb in the same region as the intermediate being observed.

Recently a vast amount of kinetic data, on absolute rate constant determination, has appeared in the literature. Although means of measurements of various parameters are now more reliable, care must still be exercised in substituting these values for obtaining absolute rate constants for those reactions for which the ratio of the reactivities with the same radical is known. Dainton has pointed out that solvated electrons can react with a molecule which can then undergo charge transfer to other molecules. This would effect the competition method and the values of the ratios of the rate constants obtained would be in error. (Dainton 1964).

1.3. Radiation Chemistry of Aqueous Solutions of Organic Compounds

From the study of a large number of aqueous solutions of organic compounds it is now known that the reactive species produced by the radiolytic decomposition of water react with the solutes to produce organic free radicals or ions:

$$\mathrm{R{-}H} + \mathrm{OH} \longrightarrow \mathrm{R.} + \mathrm{H_2O} \qquad (27)$$

$$\mathrm{R{-}H} + \mathrm{H} \longrightarrow \mathrm{R.} + \mathrm{H_2} \qquad (29)$$

$$\mathrm{CH_3.CO.CH_3} + \mathrm{e\ aq^-} \text{ ---- } \mathrm{(CH_3.CO.CH_3)^-} \qquad (39)$$

$$\mathrm{Cl.CH_2.COOH} + \mathrm{e\ aq^-} \longrightarrow \mathrm{(Cl.CH_2.COOH)^-} \qquad (40)$$

These radicals and ions can dimerise, disproportionate or react with other solutes:

$$\mathrm{R.} + \mathrm{R.} \longrightarrow \mathrm{R{-}R} \qquad (32)$$

$$\mathrm{(Cl.CH_2.COOH)^-} \longrightarrow \mathrm{Cl^-} + \mathrm{.CH_2.COOH} \qquad (8)$$

$$\mathrm{(CH_3.CO.CH_3)^-} \xrightarrow{\mathrm{H^+}} \mathrm{CH_3.C.OH.CH_3} \qquad (40)$$

$$\mathrm{R.} + \mathrm{O_2} \longrightarrow \mathrm{RO_2.} \qquad (28)$$

$$\mathrm{H} + \mathrm{O_2} \longrightarrow \mathrm{HO_2.} \qquad (25)$$

$$\mathrm{HO_2.} + \mathrm{HO_2.} \longrightarrow \mathrm{H_2O_2} + \mathrm{O_2} \qquad (31)$$

In deaerated solutions, hydrogen is usually formed in large yields as hydrogen atoms may dehydrogenate the organic solute according to reaction (29). The hydrogen yields increase in acidic solution as all of the reducing radicals exist in the form of hydrogen atoms. In the case of unsaturated organic compounds, both hydrogen atoms and hydroxyl radicals have the possibility of adding on to the unsaturated bond, as well as being involved in the abstraction reactions. In the presence of dissolved oxygen, the organic radicals react with oxygen giving organic peroxy radicals, which in further reactions produce stable organic products; aldehydes, organic acids, organic alcohols, organic peroxides. Hydrogen peroxide is often also formed during these reactions. Thus the presence of oxygen can lead to both quantitative and qualitative changes in the distribution of the products. A comparison of the nature and yields of the products in deaerated and oxygenated aqueous solutions of ethanol provides a typical example, (Jayson, Scholes and Weiss 1957).

G-values of various products at pH 1.2 .

Product	Deaerated solution	Oxygenated solution
H_2	4.2	0.6
H_2O_2	0.6	4.15
$CH_3.CHO$	1.90	2.6
Glycol	1.65	0.0

Another aspect of the radiolysis of aqueous solutions of organic compounds is the formation of hydrogen peroxide. The following table gives the radiation yields of hydrogen peroxide in some oxygenated aqueous solutions of organic compounds at pH 1.2, (Haissinsky 1963).

Compound	G (H_2O_2)
methane	2.9

acetylene	2.8
ethylene	2.8
propylene	1.2
formic acid	3.4
chloroacetic acid	2.65
ethanol	4.15
benzene	2.8

Hydrogen peroxide yield from the recombination of HO_2 radicals and the molecular processes would be $\frac{1}{2}\ G_H + G_{H_2O_2} = 2.6$. Departures from this value indicate, in the case of low values, participation of HO_2 radicals in reactions other than forming hydrogen peroxide(or the reaction of e aq^- or H with the solute). higher values of $G(H_2O_2)$, are obtained, when organic peroxy radicals also produce hydrogen peroxide. Under these conditions a maximum yield of $G(H_2O_2) = \frac{1}{2}\ (G_H + G_{OH}) + G_{H_2O_2}$ can be expected.

In some instances, radiolysis of aqueous solutions of organic compounds was pursued to determine the yields of radicals and molecular products produced in the irradiated water. An example of this kind of study is provided by the radiolysis of aqueous solutions of ethanol(Jayson, Scholes and Weiss 1957). The proposed mechanisms, on the basis of which the relation between yields of observed products and primary species were worked out, are by no means confirmed and in most cases, represent overall stoichiometry of the system.

$$CH_3.CH_2.OH + OH \longrightarrow CH_3.\dot{C}H.OH + H_2O \qquad (41)$$

$$CH_3.\dot{C}H.OH + O_2 \longrightarrow CH_3.CH(OH).O_2. \qquad (42)$$

$$CH_3.CH(OH).O_2. + HO_2. \longrightarrow CH_3.CHO + H_2O_2 + O_2 \qquad (43)$$

$$H + O_2 \text{--------} HO_2 \longrightarrow H_2O_2 + O_2 \qquad (25\ \&31)$$

From this reaction sequence, $G(CH_3.CHO) = G_{OH}$ and $G(H_2O_2) = \frac{1}{2} G_H + \frac{1}{2} G_{OH} + G_{H_2O_2}$. A detailed knowledge of the intermediate reactions of such organic peroxy radicals is of fundamental importance to the understanding of radiation-induced oxidation of organic compounds. The organic peroxy radicals derived from hydrocarbons are the simplest and in the past some progress has been made in understanding the reactions of alkyl peroxy radicals in both the gas phase and aqueous solution studies.

Radiation chemistry of aliphatic hydrocarbons in aqueous solutions.

The literature on the radiation chemistry of aqueous solutions is extensive but comparatively little published work has appeared on the radiation chemistry of aliphatic hydrocarbons in aqueous solutions. The radiation-induced oxidation of methane, iso-butane, cyclohexane, acetylene, ethylene and propylene in aqueous solution has been studied, products being carbonyl compounds, organic acids, alcohols, organic peroxides and hydrogen peroxide. Most of these systems were not investigated in detail and in the others no satisfactory mechanisms were proposed for the formation of the observed products.

Radiolysis of methane-oxygen aqueous solutions showed that methyl hydroperoxide, formaldehyde, formic acid and hydrogen peroxide were the main products (Johnson and Weiss 1955) and (Thomson ; unpublished results) . G (total organic products) = 1.45 in neutral solutions suggested that only hydroxyl radicals were taking part in the dehydrogenation of methane. The scavenging of radicals in acidic solutions seemed to be even less efficient; G (organic product) was lower than neutral solutions. Decrease in pH of the solution resulted in the decreased yield of methyl hydroperoxide and formaldehyde. No methyl hydroperoxide was detected at pH 1.2, where G (formic acid) = 0.48 and formaldehyde, G = 0.6, were the main products. The maximum measured G (H_2O_2) = 3.0 was at pH 1.5 and changes in pH on either side decreased this value. All the observed organic products were explained in terms of reactions of methyl peroxy radicals:

$$CH_4 \quad + \quad OH \xrightarrow{\hspace{4em}} CH_3. \quad + \quad H_2O \qquad (44)$$

$$CH_3. \quad + \quad O_2 \xrightarrow{\hspace{4em}} CH_3.OO. \qquad (45)$$

$$CH_3.O_2. \xrightarrow{\hspace{4em}} \text{organic products}$$

$$H \quad + \quad O_2 \xrightarrow{\hspace{4em}} HO_2 \qquad (25)$$

$$2\,HO_2 \xrightarrow{\hspace{4em}} H_2O_2 \quad + \quad O_2 \qquad (31)$$

The pH dependence of methyl hydroperoxide formation was explained by reaction of O_2^- ion with methyl peroxy radicals,

$$CH_3.O_2 \quad + \quad O_2^- \xrightarrow{\hspace{4em}} CH_3.OO^-_{:} \quad + +O_2 \qquad (46)$$

$$CH_3.O_2^- \quad + \quad H^+ \xrightarrow{\hspace{4em}} CH_3OOH \qquad (47)$$

There is a large product deficiency revealed in these studies and it is apparent that this could be due to either an undetected product (e.g. methanol) or to the low reactivity of methane towards OH radicals.

Radiolysis of aqueous solutions of iso-butane-oxygen mixtures gave formaldehyde, iso-butyraldehyde, acetone, t-butyl hydroperoxide and hydrogen peroxide (Clay, private communication). The formation of t-butyl hydroperoxide was explained by the reactions of alkyl peroxy radicals derived from iso-butane, with HO_2 radicals:

$$RO_2. \quad + \quad HO_2. \xrightarrow{\hspace{4em}} ROOH \quad + \quad O_2 \qquad (48)$$

However, little systematic work appears to have been done in this system. It is interesting to note that a major fraction of the OH radicals appear to react with the methyl hydrogens in this compound. The OH radical is known to be fairly non specific in its site of attack, a reflection presumably of the strong HO-H bond compared with C-H bonds. In the case of iso-butane, the statistical effect of the methyl hydrogens must outweigh the effect of weak tertiary C-H bond in determining the site of attack.

Phung and Burton irradiated cyclohexane aqueous solutions and from the results obtained in deaerated solutions concluded that all the hydrogen atoms, in addition to OH radicals, took part in the dehydrogenation of the cyclohexane (Phung and Burton 1957). In oxygenated solutions, G (- cyclohexane) decreased considerably but the authors could not explain large oxygen uptake, G ($-O_2$) = 5.4. Some of this yield was presumably from hydrogen atoms giving hydrogen peroxide by reactions (25) and (31), but G (hydrogen peroxide) values were not reported.

Unsaturated hydrocarbons.

Unsaturated hydrocarbons have been more thoroughly investigated than saturated hydrocarbons and it appears that OH radical addition reactions are more important than OH radical abstraction reactions. The radiation chemistry of ethylene-oxygen aqueous solutions has been studied at both atmospheric and high gas pressures. Henley and coworkers observed G-values of aldehyde production as high as 200 from ethylene-oxygen mixtures (1:1) dissolved in water under pressures ranging from 12 to 50 atm (Henley 1955). Analysis of the irradiated solutions showed that about 25 % of the aldehyde yield was formaldehyde and the remaining was assumed to be acetaldehyde. Alcohols, organic acids, organic peroxides and hydrogen peroxide were also formed in minor quantities. Weiss and coworkers investigated the same system and showed that occurrence of chain reactions at ethylene- oxygen pressures less than 10 atm was doubtful (Clay 1958). In deaerated ethylene aqueous solutions, an oily polymer was the main product, acetaldehyde, butyraldehyde and hydrogen peroxide were also formed in G-values less than 1. The yields of the products were pH dependent and on the whole decreased with increase in pH. Irradiations in the presence of adequate concentrations of oxygen, yielded formaldehyde, acetaldehyde hydroxyethanal, an unidentified organic peroxide and hydrogen peroxide. The organic peroxide was formed in G-values less than 0.4. At pH 5.5, G ($CH_3.CHO + HCHO$) = 1.3, G ($HO.CH_2.CHO$) = 2.0 and G (H_2O_2) = 2.6 were determined. Ethylene-oxygen pressures upto 10 atm did not induce any chain reaction; there was no change in the G-values of the principal products with increase in gas pressure. At pH 1.2 the major products, acetaldehyde and hydroxyethanal, were formed in almost equal quantities and as the pH was increased, the yields of these products decreased and that of formaldehyde increased. G (total organic products) decreased from 5.9 to 3.6, when pH was changed from 1.2 to 5.5. It is apparent that observed yields of organic products were higher than G_{OH} in both neutral and acidic solutions. Hydrogen atoms could not have taken part in increasing the product yield as under these conditions all of them would be scavenged by the oxygen. It is likely that a short chain reaction is responsible for the observed increase but the authors did not find any concentration dependence, which is a characteristic of chain reactions.

Francis conducted further studies on ethylene solutions at high gas pressures in a more systematic way and showed that in solutions containing oxygen up to a total Cullen pressure of 33 atm, no chain reaction occurred (Francis, 1963 & 1965). Results of the experiments in deaerated solutions were similar to those obtained by Weiss and his colleagues in that polymerisation of ethylene was the predominant process under these conditions. Detectable quantities of acetaldehyde, higher aldehydes and hydrogen peroxide were also formed. However, remarkably different results were obtained in the radiolysis of oxygenated solutions:

G-values of products (Francis)

Total gas pressure = 10 atm. O_2% in solution = 10

pH	HCHO	$CH_3.CHO$	$HO.CH_2.CHO$	$CH_3.CH_2.CHO$	ROOH	H_2O_2
1.2	0.61	5.15	0.01	0.41	4.14	0.79
5.5	0.34	2.32	0.01	0.65	4.14	0.59

Total gas pressure = 33 atm Oxygen in solution = 40 %

pH	HCHO	$CH_3.CHO$	$HO.CH_2.CHO$	$CH_3.CH_2.CHO$	ROOH	H_2O_2
1.2	2.43	4.46	0.01	0.28	3.08	0.9
5.5	0.51	1.25	0.01	0.13	4.14	1.26

G values of products (Weiss)

Total pressure 1 - 10 atm. Oxygen in solution = 50 % .

pH	HCHO	$CH_3.CHO$	$HO.CH_2.CHO$	$CH_3.CH_2.CHO$	ROOH	H_2O_2
1.2	0.6	2.4	2.4	0.0	0.3	2.4
5.5	1.0	0.3	2.0	0.0	0.4	2.6

From the above tables it can be seen that whereas hydroxyethanal was the major product in the experiments of Weiss, it was formed in almost negligible quantities in the experiments of Francis. In the work of Francis an organic peroxide (identified as β-hydroxy ethyl hydroperoxide) was formed in G values as high as 4.14 but Weiss found that G (organic peroxide) was of the order of 0.4 or less. Francis also showed that apart from formaldehyde and acetaldehyde, propionaldehyde was formed in significant yields. This product was not detected by Weiss and coworkers. In both the works however, it was shown that increase in oxygen concentration at a given pH and ethylene concentration, decreased G-values of aldehydic products but those of organic peroxide and hydrogen peroxide were substantially the same at all oxygen concentrations investigated.

There are fundamental differences in the mechanisms proposed by the two group of workers. Weiss and coworkers considered that the most probable initial reaction was the addition of an OH radical to the double bond:

$$CH_2{:}CH_2 \quad + \quad OH \longrightarrow HO.CH_2.CH_2. \qquad (49)$$

The hydrogen abstraction reaction (50) was considered unlikely on energetic grounds:

$$CH_2{:}CH_2 \quad + \quad OH \longrightarrow CH_2{:}CH. \quad + \quad H_2O \qquad (50)$$

In both the studies, addition of hydrogen atoms to ethylene double bonds in the absence of oxygen, was assumed:

$$CH_2{:}CH_2 \quad + \quad H \longrightarrow CH_3.CH_2. \qquad (51)$$

To explain the apparentlyl high yields of the organic products compared with G_{OH}, reactions (52) and (53) were proposed by Weiss:

$$CH_3.CH_2. + O_2 \longrightarrow CH_3.CH_2O_2. \qquad (52)$$

$$CH_2:CH_2 + HO_2. \xrightarrow{O_2} HO_2.CH_2.CH_2.O_2 \qquad (53)$$

Radiolysis in the presence of Fe^{2+} showed that acetaldehyde was a major product but, that in the Fenton's reagent-initiated reaction no acetaldehyde was formed. These experiments were proposed to support the participation of $HO_2.$ radicals or hydrogen atoms in the formation of acetaldehyde. It is now known that reaction between H atoms and oxygen is about 200 times faster than reaction (51) and therefore under the conditions of their experiments, no hydrogen atom can add on to the ethylene double bond. (Callear and Pereira 1963)

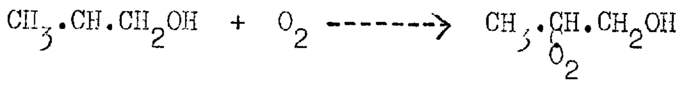
Francis also proposed several mechanisms for the formation of the observed products. His results however, indicated that a large proportion of hydroxyl radicals should also abstract hydrogen from the ethylene according to reaction (50). From the pulse radiolysis studies he obtained some evidence for the formation of β- hydroxy ethyl peroxy radicals and also showed that they reacted in bimolecular processes:

$$2\ HO.CH_2.CH_2.O_2 \longrightarrow \text{products}$$

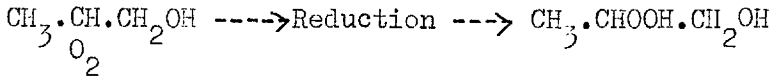
These substituted alkyl peroxy radicals were thought to be giving rise to the observed organic products.

Irradiation of propylene-oxygen aqueous solutions yielded an organic peroxide as the major product (Clay 1959). The total aldehyde yield was made up of small quantities of formaldehyde, acetaldehyde and propionaldehyde. Formic acid was also among the products of the radiolysis. The organic peroxide was characterised as $CH_3.CHOOH.CH_2OH$ and its formation was explained by following sequence of reactions:

$$CH_3.\dot{C}H:CH_2 + OH \longrightarrow CH_3.\dot{C}H.CH_2OH \qquad (54)$$



$$CH_3.CH.CH_2OH + O_2 \dashrightarrow CH_3.\underset{O_2}{CH}.CH_2OH \qquad (55)$$



$$CH_3.\underset{O_2}{CH}.CH_2OH \dashrightarrow \text{Reduction} \dashrightarrow CH_3.CHOOH.CH_2OH \qquad (56)$$

Experimental evidence was not enough to describe the nature of the reduction step. However, between pH 1 - 5, G (hydroperoxide) was essentially constant suggesting that reduction step involved both HO_2 and O_2^- ion or, that this product was produced via reactions between organic alkoxy and peroxy radicals. It has been shown that photolysis of hydrogen peroxide solutions in the presence of propylene oxygen mixtures resulted in the formation of an organic peroxide. This peroxide has not been identified but it is likely to be the one found in the radiolysis of propylene-oxygen aqueous solutions. Since it is probable that no HO_2 radicals are formed in the photolysis the reduction step must not involve HO_2 or O_2^- (Clay and Khan, private communication).

1.4. Present Work

From the survey of the previous work done on the oxidation of hydrocarbons in aqueous solutions, it emerges clearly that an understanding of the reactions of organic peroxy radicals is absolutely vital for further progress in this field. Methane and ethane are the simplest hydrocarbons and the study of their oxidation in aqueous solutions has been the major preoccupation in the present work. Most of the information has been obtained by the radiolysis of methane-oxygen and ethane-oxygen aqueous solutions but photolysis of hydrogen peroxide solutions containing methane-oxygen or ethane-oxygen mixtures has also helped to clarify some aspects of reactions of ethyl and methyl peroxy radicals.

In view of the contradictory nature of the results of radiolysis of ethylene-oxygen aqueous solutions, it was desirable to study the hydroxyl radical initiated oxidation of ethylene by photolysis of hydrogen peroxide solutions. It was hoped by these means to observe product formation under conditions where H atoms and hydrated electrons were absent.

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CHAPTER 2

EXPERIMENTAL

2.1. Experimental Arrangements

For the purpose of preparation of the aqueous solution samples for subsequent irradiation or photolysis a general purpose vacuum line was built. It consisted of a gas purification and storage sections, a pumping section and a gas analysis section. Solutions of the gases in water were prepared in a 1 litre capacity round bottom flask which was filled with 300 ml of water⊕ and then connected to the vacuum line through a B 14 cone and socket joint. The water was deaerated by alternate evacuation and shaking. The gases were then filled in at the required pressures and the vessel was detached from the line and shaken vigorously for about 10 minutes. Gas analysis of the solutions showed that this procedure resulted in a satisfactory equilibration. The irradiation vessel, capacity 100 ml, was made of Pyrex glass and was cylindrical in shape. The vessel could be placed in a hole around the radiation source in a position of fixed geometry. For the radiolysis an 800 curies Co-60 source was used. The dose rate to the samples could only be altered by the adjustment of the distance between the source and the sample. High pressure irradiations were carried out in a stainless steel pressure vessel, which was about 9" high and 1.8" in diameter. The inlet and the outlet of the gases was controlled by two needle valves fixed in the cap of the pressure vessel. On the cap of the pressure valve was also fixed a pressure gauge reading between 0.0 and 200.0 p.s.i. The cap was screwed on to the main body through an '0' ring to make it pressure tight. To avoid contact with the metal surface, the solution of the gases in water was prepared in a glass vessel, capacity 150 ml, placed at the bottom of the pressure vessel. On the lower side of the cap was fixed a glass capillary which dipped into the solution when it was fixed on to the main body. This allowed the gases to be bubbled through the solution and helped to achieve quick saturation.

⊕ Low pH was adjusted with sulphuric acid.

High pH was adjusted with sodium hydroxide.

The first gas to be passed was bubbled into solution for 15 minutes to drive all the air out. The outlet needle valve was then closed and the gases filled in at required pressures, as indicated by the gauge. The pressure vessel was gently shaken to achieve maximum saturation and since vigorous shaking was not possible the vessel was allowed to stay overnight prior to irradiation. The dosimetry was done by taking 100 ml of dosimetry solution in the glass vessel and irradiating the pressure vessel in a fixed position.

To study the effect of temperature changes on the yields of various products formed in the radiolysis of ethane-oxygen system the irradiation vessel was thermostatted in a simple open mouth Thermos flask, containing water at a fixed temperature. After about 15 minutes the temperature of the solution in the irradiation vessel reached that of the bath and then the whole set up was placed in the radiation source. Since the time of irradiation was of the order of 10 - 45 minutes, the temperature of the bath did not change by more than one degree.

For photolysis a Hanovia medium pressure mercury lamp was used. Water decomposing radiations below 1875 A^o were cut off by imposing a 5" thickness of 0.1 M sodium chloride solution between the source and the sample. The solutions were photolysed in a silica vessel, capacity 100 ml. Actinometry was done by photolysing hydrogen peroxide solutions in the presence of allyl alcohol.

2.2. MATERIALS

All solutions used in this work were prepared in triply distilled water: prepared by twice distilling the distilled water once from alkaline potassium permanganate and then from acidic potassium dichromate. The pH of the resulting water was about 5.7. This value was due to the dissolved carbon dioxide from the air and its concentration in the water was of the order of 10^{-5} M.

On evacuation of water, particularly in the acidic solutions, this value would be still lower and in aqueous solutions containing 10^{-4} to 10^{-2} M reactant gases, methane, ethane, oxygen and other radical scavengers as nitrous oxide, the effect on the yields of the products due to carbon dioxide would be negligible.

Ethane was supplied by British Oxygen Company (B.O.C.). Gas chromatographic analysis of the gas from the cylinder showed it to be about 96 % ethane, 2.5 % ethylene and the remaining, propane butane and methane. Since both propane and ethylene are more soluble in water than ethane and are possibly more reactive, it was imperative to purify the gas from the cylinder before use. Ethylene was removed by allowing the gas from the cylinder to liquify on molecular sieve (Type A 1/8", B.D.H.) contained in a trap cooled by liquid nitrogen. Vacuum was then applied to remove higher vapour pressure methane (B.P. - 161°) and the ethylene which was not adsorbed by the molecular sieve. The liquid nitrogen trap was then replaced by methanol-ethanol slush trap maintained at - 90°C to - 100°C. The fraction obtained between these temperatures was collected in a storage vessel cooled by liquid nitrogen. Propane (B.P. -42°C) and higher hydrocarbons stayed behind in the slush trap. Analysis of the purified gas showed it to be 99.99 % ethane and remaining propane.

Ethylene, supplied by B.O.C. was 99.8 % pure and was used without further purification.

Methane was supplied by L'Air Liquide of Belgium. Gas chromatographic analysis of the gas from the cylinder showed it to be 99.99 % pure and was used as such.

Hydrogen was supplied by B.O.C. and its purity being better than 99.8 % was used straight from the cylinder.

Oxygen and nitrous oxide were supplied by B.O.C. and were of medical grade of purity.

Other chemicals and laboratory reagents were supplied by

Hopkin and Williams Ltd,Essex and were of Analar grade of purity.

2.3. DOSIMETRY

Throughout this work the quantity of energy absorbed by the aqueous solutions, exposed to gamma radiations was determined by the Fricke Dosimeter. 1 g of ferrous ammonium sulphate and 0.05 g of sodium chloride were dissolved in 200 ml of water. 3.2 ml of concentrated sulphuric acid, specific gravity 1.84, were added and volume made upto 1 litre. The cleaned and dried irradiation vessel was filled completely with this solution and irradiated for 5, 10 and 15 minutes. The optical density of the irradiated solution was measured against the original unirradiated solution at 304 mu in 1 cm silica cells. The temperature of the solution in the cell was noted at the same time and the dose rate at the irradiation position was calculated using the following equation:

$$\text{Dose in rads/ time} = 2.94 \times 10^{4}(1- 0.007t) \times \text{O.D.}$$

Where O.D. is the observed optical density and t is the temperature of the solution. For the purpose of calculation of G values of various products dose in rads was converted to electron volts by the use of following expression:

$$10^{14}\ \text{eV/g} = 1.6\ \text{rad}$$

2.4. Analysis of The Products

Aldehydes

Acetaldehyde and formaldehyde were identified by the paper chromatography of aldehyde 2:4-dinitro phenyl hydrazones (Gasparic and Vecera 1957). 5 ml of 0.25 % 2:4-dinitro phenyl hydrazine (D.N.P.H.) in 30 % perchloric acid were added to 40 ml of irradiated or photolysed solution and allowed to stand for 30 minutes. The aldehyde phenyl hydrazone formed was extracted with 20 ml of carbon tetrachloride and the organic extract was washed with 20 ml of 10 % perchloric acid solution twice. Excess acid was then removed by washing the organic extract with water. The organic extract was then treated with anhydrous sodium sulphate to remove moisture and carbon tetrachloride was evaporated off under reduced pressure. The residue was dissolved in a limited quantity of absolute alcohol and a small drop of this solution was spotted on to the strip of chromatography paper which had been previously treated with 10 % dimethyl formamide in ethanol and allowed to dry in air. The chromatography paper was then run with a spot of acetaldehyde and formaldehyde hydrazone as reference, using dimethyl formamide saturated hexane as the mobile phase.

Acetaldehyde was estimated by the method of Johnson and Scholes (Johnson and Scholes 1954). 2 ml of 0.25 % D.N.P.H. solution in 30 % perchloric acid were added to a 10 ml aliquot containing 10^{-7} to 10^{-6} moles of acetaldehyde and allowed to stand for 30 minutes. The acetaldehyde hydrazone formed was extracted with 10 ml of carbon tetrachloride, the organic layer was separated in a separating funnel and mixed with 10 ml of absolute alcohol. This solution was then treated with 1 ml of 0.1 N sodium hydroxide in ethanol and shaken vigorously. A stop watch was started at the same time. The wine red colour produced was measured after two minutes against water as blank at 430 mu. A blank observation was also carried out using 10 ml of water and 2 ml of D.N.P.H reagent. A method based on the oxidation of acetaldehyde in aqueous solution (Siegel and Weiss 1954) was used to prepare a standard solution of acetaldehyde to calibrate the spectrophotometer. Acetaldehyde was determined in irradiated and photolysed solutions in the same manner. Ethyl hydroperoxide, a product of the radiolysis of ethane-oxygen aqueous solutions did not interfere in the determination of acetaldehyde.

Quantitative determination of formaldehyde was carried out by the same method as described for acetaldehyde. A crude sample of formaldehyde hydrazone was prepared by reacting dilute formaldehyde solution with the D.N.P.H. reagent. The product thus obtained was washed with water and dried at 50°C. It was then crystallised three times from absolute alcohol and carefully dried at 50°C in an oven. A known weight of the dried product was dissolved in carbon tetrachloride and this standard solution of formaldehyde hydrazone was used to prepare the calibration curve for its determination. Formaldehyde was also estimated on occasions by the chromotropic acid method (Satterfield and others 1954). The reagent was prepared by dissolving 0.2 g of chromotropic acid in 10 ml of water and the solution filtered into a 200 ml capacity brown coloured reagent bottle. 100 ml of concentrated sulphuric acid were added and the resulting solution was placed in a cool dark place. 2 ml of aliquot containing formaldehyde were mixed with 4 ml of the reagent and heated in a boiling water bath for 30 minutes. The optical density of the purple colour produced was measured in 1 cm cells at 570 mu against 2 ml of water or original solution not containing formaldehyde and 4 ml of the chromotropic acid reagent as the blank.

Hydroxyethanal.

The determination of this product in photolysed ethylene-oxygen aqueous solutions was made by a method developed by Johnson and coworkers(Johnson 1962). 2 ml of aliquot sample were mixed with 1 ml of 10 % sulphuric acid solution and one ml of D.N.P.H. reagent (0.1 g of 2:4-dinitro phenyl hydrazine were dissolved in 50 ml of methanol and to this solution 4 ml of concentrated hydrochloric acid were added. The clear solution was then diluted to 100 ml with water) and heated in a boiling water bath for 30 minutes. The contents of the tube were cooled to room temperature and diluted with 15 ml of water. The hydrazone formed was extracted with 5 ml of methylene dichloride and the organic layer was separated from the aqueous layer by a separating funnel. 5 ml of the organic extract were evaporated to dryness and the residue was treated with 2 % v/v diethanolamine in pyridine. The dark green colour produced was measured in 1 cm cells at 580 mu against water as a blank. Calibration of the spectrophotometer was carried out by using glyoxal which gives the same hydrazone with the D.N.P.H. reagent as hydroxyethanal. Pure glyoxal in the form of sodium bisulphite was weighed as such to provide a standard solution in water (10^{-4}M). 2 ml aliquot of this solution was treated in the same way as described for hydroxyethanal. A calibration curve was prepared by using suitable concentrations of glyoxal in solution. Acetaldehyde, formaldehyde, formic acid or hydrogen peroxide present in the same solution did not interfere in the determination of hydroxyethanal. It was not known to what extent the organic hydroperoxide formed in the photolysis of ethylene-oxygen solutions interfered with the determination of hydroxyethanal.

Ethanol and methanol.

Both ethanol and methanol were identified and determined by the gas chromatography. A standard solution of ethanol or methanol (10^{-5}M) was prepared and a 100 microlitre sample, measured by standard Hamilton syringe, was injected into Perkin Elmer gas chromatography machine. A stop watch was started at the same time, the methanol peak appeared after about 8 minutes and the ethanol peak appeared after about 10 minutes. This was followed by the water peak which took about 30 minutes to clear. This was due to the large volume of the injection sample which caused water vapours to condense downstream from the detector, and restrict the flow of the carrier gas. Determination of methanol and ethanol in the irradiated and photolysed solutions was carried out in the same way. In the case of ethanol, acetaldehyde present in the same solution, did not interfere; the ethanol peak, as in the standard sample, appeared after 10 minutes. The acetaldehyde peak appeared after 2 minutes and 30 seconds and the fact that it was due to acetaldehyde, was checked by adding acetaldehyde in the standard sample as well. In the case of methanol, formaldehyde present in the same solutions did interfere and therefore had to be removed. This was achieved by distilling the irradiated or photolysed solution over D.N.P.H. reagent, as described under formaldehyde determination. A peak due to methanol as in the reference sample, appeared after 8 minutes but was not very well defined. From the peak heights and area considerations of not very well defined peaks an estimate of both the ethanol and methanol concentrations in the irradiated and photolysed solutions was made.

In the radiolysis and photolysis experiments carried out in acidic solutions it was necessary to remove the large quantity of sulphuric acid in order to avoid damage to the gas chromatograph. This was achieved by the vacuum distillation of the irradiated or photolysed solutions, at low temperature in order to avoid the possible decomposition of the organic products. The distillation apparatus consisted of a 'U' tube, to the horizontal part of which was attached a B 14 socket through a 2 mm vacuum tap, and the two ends of the 'U' tube were made of B 24 cones. 20 ml of the acidic solution containing decimolar sulphuric acid were taken into a 250 ml capacity round bottom flask and fixed to one end of the transfer apparatus. At the receiving end a 250 ml capacity conical flask was attached and the whole apparatus was evacuated. The receiving end was then carefully cooled in a liquid nitrogen trap. This caused all the water and volatile organic products to come over leaving behind sulphuric acid. No substantial loss of the products occured during the transfer operation. This was verified by making a test solution of the products; formaldehyde, acetaldehyde ethanol and methanol of about the same concentrations as present in the irradiated and photolysed solutions. For specification of the machine and column used in methanol and ethanol analysis see appendix section of this report.

Formic acid.

Formic acid was identified by reducing it to formaldehyde using magnesium and hydrochloric acid as the reducing agents (Grant 1948). This method is not very sensitive and concentration of the test solution by a factor of about 10 was considered necessary to analyse formic acid more accurately. 100 ml of the irradiated or photolysed solution was made alkaline with 5 drops of 0.1N sodium hydroxide and the solution was evaporated to dryness using the distillation apparatus described under the determination of alcohols. The residue in the flask was extracted twice with 5 ml of water each time. The water extract (10 ml) was transferred to a test tube and placed in an ice bath at 0°C. When the temperature of the solution reached that of the bath, it was made acidic with exactly six drops of concentrated hydrochloric acid. 2 ml from acidified solution were withdrawn for the blank observation. A strip of magnesium metal weighing about 10 mg was cleaned in dilute hydrochloric acid solution and after washing and drying placed into the solution to be reduced. After about 30 minutes the strip disappeared but the solution was allowed to stand in the ice bath for another five minutes. 2 ml of the reduced solution were mixed with 4 ml of the chromotropic acid reagent and the purple colour produced was measured as described under formaldehyde. This method was calibrated against standard formic acid solution which was prepared by titration against standard sodium hydroxide. Experience showed that reduction of formic acid to formaldehyde is a tricky operation and unless the conditions of reduction are carefully controlled large errors in the determination of formic acid would occur. It is also important to use exactly the same conditions for the blank as for the test part of the reduced solution. The presence of methyl hydroperoxide in the same solution interefered with the formic acid determination, as methyl hydroperoxide forms a sodium salt which is retained as residue in the concentration operation and contributes to the total formaldehyde yield from formic acid. Due to this difficulty formic acid could not be analysed in the radiolysis of neutral methane-oxygen aqueous solutions. Formic acid was also analysed in the photolysis of ethylene-oxygen aqueous solutions and it was established that hydroxyethanal did not interfere in this analysis However, it was found that the organic hydroperoxide formed in this system could not be removed in the concentration operation and always contributed to the observed formic acid yields. This error was corrected by using the blank containing this peroxide and treating it the same way upto the reduction step, at which point it was separated from the solution to be reduced.

Peroxides.

Four different peroxides namely hydrogen peroxide methyl hydroperoxide, ethyl hydroperoxide and hydroxy ethyl hydroperoxide were identified and quantitatively determined in this work.

Hydrogen peroxide was identified and measured by the titanium sulphate method (Eisenberg 1943). It is based on the colour reaction of hydrogen peroxide with this reagent. None of the other organic peroxides found in this work gave any colour with this reagent. The titanium sulphate solution available commercially was found to be unsatisfactory as it did not give linear calibration curve with hydrogen peroxide. In view of this difficulty titanium sulphate was prepared in the laboratory by digesting 1 g of titanium oxide (B.D.H. "Fine Chemicals") in 100 ml of concentrated sulphuric acid at 140°C. When the digestion was completed, the reaction mixture was cooled to room temperature and then carefully diluted to 300 ml with water. The resulting solution was filtered into a 500 ml capacity reagent bottle and the volume made upto 500 ml with water. A few drops of 0.1 M hydrogen peroxide were added to give the reagent a pale yellow colour and stored in a cool dark place. The colouring of the reagent was found to be necessary as otherwise the calibration curve did not pass through the origin. It was found necessary to shake the reagent before use and also to check the usefulness of the reagent against standard hydrogen peroxide solution now and then. The reagent can be used in acidic, neutral and alkaline media.

A standard solution of hydrogen peroxide was prepared by titration against potassium iodide-potassium iodate solution (Vogel, Quantitative Inorganic Analysis). The stock solution was then diluted to hydrogen peroxide concentration of the order of 10^{-4}M. 25 ml of this solution were mixed with 2 ml of the titanium sulphate reagent and the yellow colour produced was measured in 4 cm cells at 410 mu against 2 ml of titanium sulphate reagent plus 25 ml of the solution used as the blank. The calibration curve was prepared by using suitable concentrations of standard hydrogen peroxide solution..

The identification of methyl hydroperoxide formed in the radiolysis of methane-oxygen aqueous solutions was made by studying its kinetics with iodide ions in aqueous solutions, and also by its decomposition to formaldehyde in the presence of the chromotropic acid reagent. In both the cases a synthetic sample of methyl hydroperoxide was prepared and used as a reference. Methyl hydroperoxide was prepared by reacting dimethyl sulphate with alkaline solution of hydrogen peroxide (Williams and Mosher 1954). 5 ml of dimethyl sulphate and 5 ml of N sodium hydroxide were mixed in a 250 ml capacity conical flask and shaken vigorously for 10 minutes. The reaction mixture was then allowed to stand in warm water bath (30°C) for about 30 minutes. The organic layer was then separated from the aqueous layer by a separating funnel.

The aqueous layer was then cooled in an ice bath to 0°C and 5 ml of 30 % hydrogen peroxide were added drop by drop, the reaction mixture was allowed to stand for 30 minutes. 5 ml of this solution were diluted to 200 ml and excess alkali was neutralised by dilute sulphuric acid. Excess hydrogen peroxide was removed by distilling a suitable quantity of the solution over the titanium sulphate reagent under vacuum. The distillate did not contain any formaldehyde as indicated by the D.N.P.H. reagent. Dimethyl peroxide is also produced by this method but it does not react with the iodide reagent. The method described above is a fairly general method for the preparation of organic hydroperoxides and was also used for preparing ethyl hydroperoxide from diethyl sulphate.

The iodide reagent used for the kinetic runs was prepared by mixing equal volumes of two solutions, one prepared by dissolving 33 g of potassium iodide, 1 g of sodium hydroxide and 10 ml of 1 % solution of ammonium molybedate (as the catalyst) in 500 ml of water and the other prepared by dissolving 10 g of potassium hydrogen phthalate in 500 ml of water. The required amounts of these solutions were mixed just before use.

25 ml of the irradiated solution solution containing organic hydroperoxide and hydrogen peroxide were distilled over the titanium sulphate reagent and the distillate was again tested for hydrogen peroxide by the titanium sulphate reagent. 5 ml of this solution and 5 ml of the iodide reagent were mixed and a stop watch was started at the same time. The optical density of I_3^- ions formed by the reaction

$$ROOH + I^- \xrightarrow{I_2} I_3^- + \text{organic products}$$

was followed by the spectrophotometer at 353 mu. Optical density measurements were made at suitable intervals of time and were extended beyond the time of half completion of the reaction. The final optical density corresponding to the initial concentration of the peroxide was measured after about 10 hours. This was the general method for studying the kinetics of all three organic peroxide occuring in the present work. For the purpose of comparison, both methyl and ethyl hydroperoxides were prepared in the laboratory and their kinetics was studied in the same way.

The kinetic data obtained from the ethyl hydroperoxide prepared in the laboratory and the organic hydroperoxide found in the radiolysis of ethane-oxygen aqueous solutions showed good agreement but this was not satisfactory in the case of methyl hydroperoxide and the organic hydroperoxide formed in the radiolysis of methane-oxygen aqueous solutions. In view of this uncertainty an alternative method for the positive identification of the organic peroxide formed in the radiolysis of methane-oxygen aqueous SOLUTIONS was developed. The method is based on the decomposition of methyl hydroperoxide to formaldehyde in the presence of the chromotropic acid reagent. 25 ml of the irradiated solution were distilled over the titanium sulphate reagent to remove hydrogen peroxide. The distillate was divided into 3 parts, to one part (5 ml) 5 ml of the iodide reagent were added and after 10 hours optical density was measured. This provided total aoncentration of the peroxide before decomposition. To the second part (10 ml) 2 ml of the D.N.P.H. reagent was added and after 30 minutes analysed for free formaldehyde in the solution. To the third part (2 ml) 4 ml of the chromotropic acid reagent were added and the resulting mixture heated in a water bath at 100°C for 30 minutes. The purple colour produced was measured as described for formaldehyde analysis.

From this step, the formaldehyde produced by the decomposition of methyl hydroperoxide was calculated. The synthetic methyl hydroperoxide was treated in a similar way and the ratio of methyl hydroperoxide decomposed to formaldehyde formed showed good agreement (Appendix 6) It was shown that ethyl hydroperoxide treated in the same way did not decompose to formaldehyde.

Hearne and Hummel reported that when methyl hydroperoxide solutions were diluted below 3.3×10^{-5}M, methyl hydroperoxide decomposed to hydrogen peroxide but the total peroxide concentration of the solution, measured by the iodide reagent, was unchanged. A similar study was conducted in the present work and it was shown that whereas methyl hydroperoxide solutions containing 10^{-8} moles/ml of methyl hydroperoxide decomposed slowly, no enhanced decomposition was observed at or below 3.3×10^{-5}M methyl hydroperoxide. It was also shown that methyl hydroperoxide on decomposition in dilute aqueous solutions does not produce hydrogen peroxide. This can be seen from the optical density-time plots (Fig 17). Considering Hearne and Hummel's work these plots would not be linear for pure methyl hydroperoxide but give two lines representing the different rates of reaction of methyl hydroperoxide and hydrogen peroxide (Hearne and Hummel 1965).

The analysis of the total peroxides ($ROOH + H_2O_2$) was carried out by the iodide method (Hochanadel 1952). 5 ml of the irradiated solution were mixed with 5 ml of the iodide reagent and allowed to stand for 10 hours. The optical density of the pale yellow colour produced was measured in 1 cm cells at 353 mu against 5 ml of water + 5 ml of the iodide reagent as a blank. This procedure was also used to prepare a calibration curve for standard hydrogen peroxide solutions. The same calibration curve was used for the determination of organic hydroperoxides formed in the present work. To determine the concentration of the organic peroxide and hydrogen peroxide separately, the following two modifications were found convenient. The test solution was divided into two parts. In the first part, hydrogen peroxide was destroyed by adding a drop of catalase enzyme, and the organic peroxide which is stable towards catalase, was measured with the iodide method. In the second part total peroxide concentration of the solution was determined as before and from these two quantities the concentration of hydrogen peroxide was calculated by subtraction. The second method was more reliable and was preferred when large quantities of the test solutions were available. The total peroxides were again determined by the iodide method and the hydrogen peroxide determined by the titanium sulphate method. Careful use of both the methods provided satisfactory results.

Nitrite.

Two reagents are required. Reagent (A); 0.6 g of 1-naphthyl amine was dissolved in 95 ml of hot water and the volume made upto 100 ml by adding 5 ml of glacial acetic acid. Reagent (B); 1.08 g of sulphanilic acid dissolved in 80 ml of water and volume made upto 100 ml by adding 20 ml of glacial acetic acid. A standard solution of the order of 10^{-5}M with respect to nitrite was prepared by dissolving sodium nitrite in water. To a 10 ml aliquot of this solution were added 2 ml of the reagent (A) and 2 ml of the reagent (B), strictly in that order. The contents of the tube were shaken and allowed to stand for 15 minutes. The optical density of the pink colour produced was measured in 1 cm cells at 530 mu. A blank observation was made using 10 ml of water and 2 ml each of reagent (A) and (B). The irradiated solutions were subjected to the same treatment for the determination of nitrite produced (Endres and Kaufman 1937).

Various factors, used in this work for converting the observed optical densities of various organic and inorganic products into concentrations are given in Appendix 7 of this report.

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CHAPTER 3

RESULTS

3.1. Radiolysis of Ethane-Oxygen Aqueous Solutions

Preliminary experiments showed that acetaldehyde, ethanol ethyl hydroperoxide and hydrogen peroxide were the main products of the radiolysis of ethane-oxygen aqueous solutions. In subsequent experiments, the effects of pH and electron scavenging solutes (nitrous oxide, hydrogen peroxide and nitrate ions) on the yields of these products were investigated. The G values of various products listed in Table 1 were calculated from the dose-yield plots (Fig.1 to 5) and also from the dose-yield tables given in the appendix. It can be seen that acetaldehyde and hydrogen peroxide were formed under all conditions of radiolysis but ethanol determinations gave positive results only in acidic solutions. Ethyl hydroperoxide was not detected in acidic solutions but it was formed in both neutral and alkaline solutions.

At pH 1.2 $G(CH_3.CHO + CH_3.CH_2OH) = 2.8$, which is in good agreement with $G_{(OH)}$ for acidic solutions. It would thus appear that acetaldehyde and ethanol were the only organic products of the radiolysis at pH 1.2. The peroxide yield G = 3.7 was entirely due to hydrogen peroxide. At pH 5.5, 10.0 and 11.0, acetaldehyde and hydrogen peroxide yields were lower than those at pH 1.2 and ethyl hydroperoxide was also detected. No ethanol was observed as the method used for its estimation was not very sensitive and could not have detected ethanol if formed with G values of less than 0.20. Large variations in the yields of acetaldehyde, ethyl hydroperoxide and hydrogen peroxide were observed at pH 5.5 radiolysis. The total yield of the organic products was internally consistent in all experiments but individual product yields showed no systematic variations. The effect of concentration of the reactant gases was studied and it was found that concentration changes upto 50 % were not responsible for such large variations in the product yields. Temperature variation

Radiolysis of Ethane-Oxygen Aqueous Solutions.

Table 1 : G values of the products.

pH	Reactants M x 10^3/L					G Values (molecules / 100 eV)				
	C_2H_6	O_2	N_2O	H_2O_2	NO_3^-	CH_3CHO	C_2H_5OH	C_2H_5OOH	H_2O_2	NO_2^-
5.5	1.0	0.7	-	-	-	1.6±0.3	-	0.9±0.3	2.0	-
1.2	1.0	0.7	-	-	-	2.4±0.2	0.44	-	3.7	-
10.0	1.0	0.7	-	-	-	1.3±0.3	-	1.3±0.3	1.7	-
11.0	1.0	0.7	-	-	-	0.6±0.2	-	1.8±0.4	0.9	-
5.5	0.91	0.3	59.0	-	-	3.1±0.2	-	0.2±0.1	3.3	-
5.5	1.0	0.7	-	8.5	-	3.0±0.2	-	0.6±0.3	-	-
5.5	1.0	0.7	-	-	100	1.6±0.3	-	1.08 ±0.3	1.72	1.2±0.3

γ-radiolysis of ethane-oxygen aqueous solutions.
pH dependence of acetaldehyde dose-yield curves.

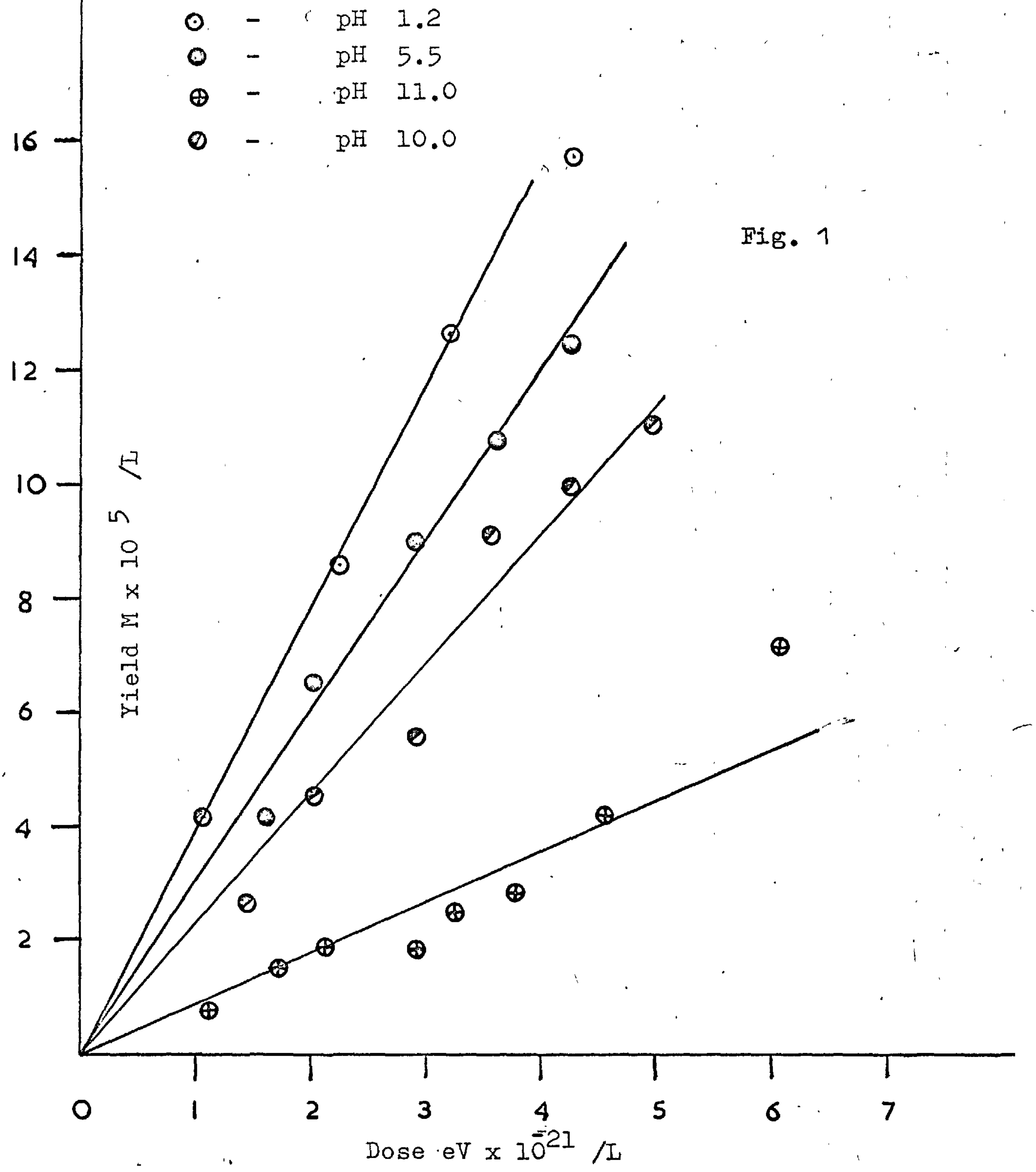


Fig. 1

γ-radiolysis of ethane-oxygen aqueous solutions.
pH dependence of ethyl hydroperoxide dose-yield curves

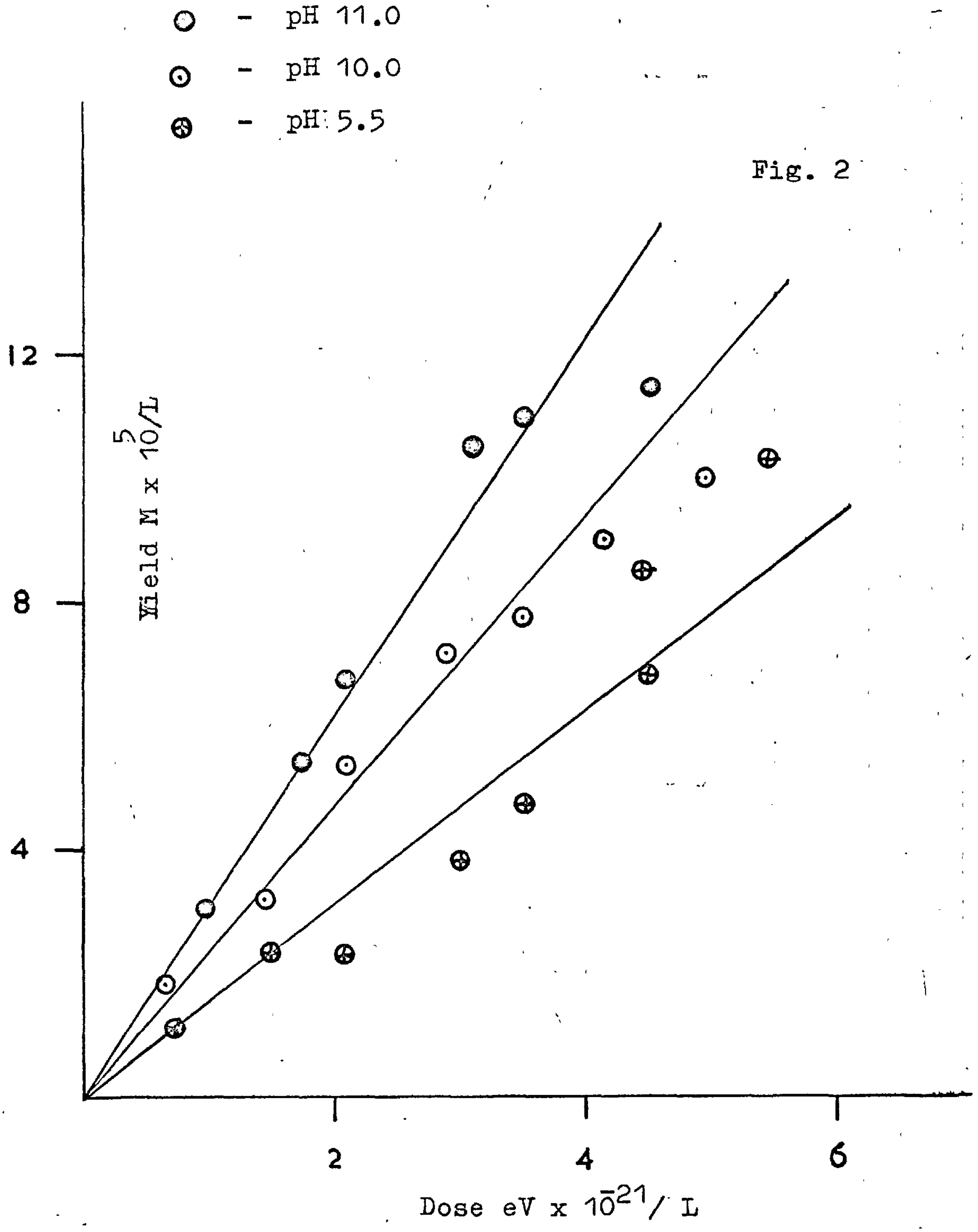


Fig. 2

γ-radiolysis of ethane-oxygen aqueous solutions.

pH dependence of hydrogen peroxide dose-yield curves.

○ - pH 1.2
⊙ - pH 5.5
⊕ - pH 10.0
\+ - pH 11.0

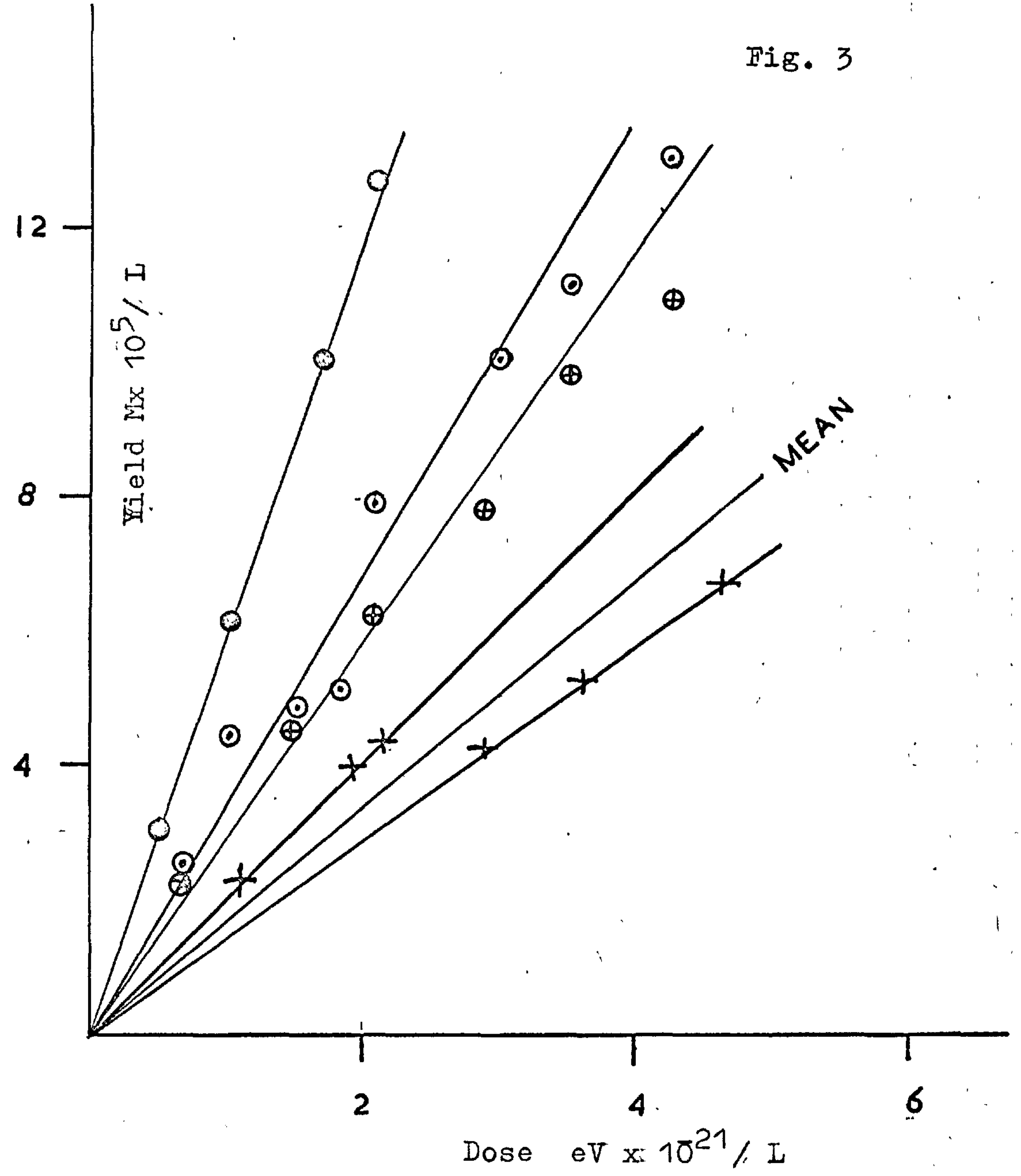


Fig. 3

γ-radiolysis of ethane-oxygen aqueous solutions. Effect of added scavengers on acetaldehyde dose-yield curves.

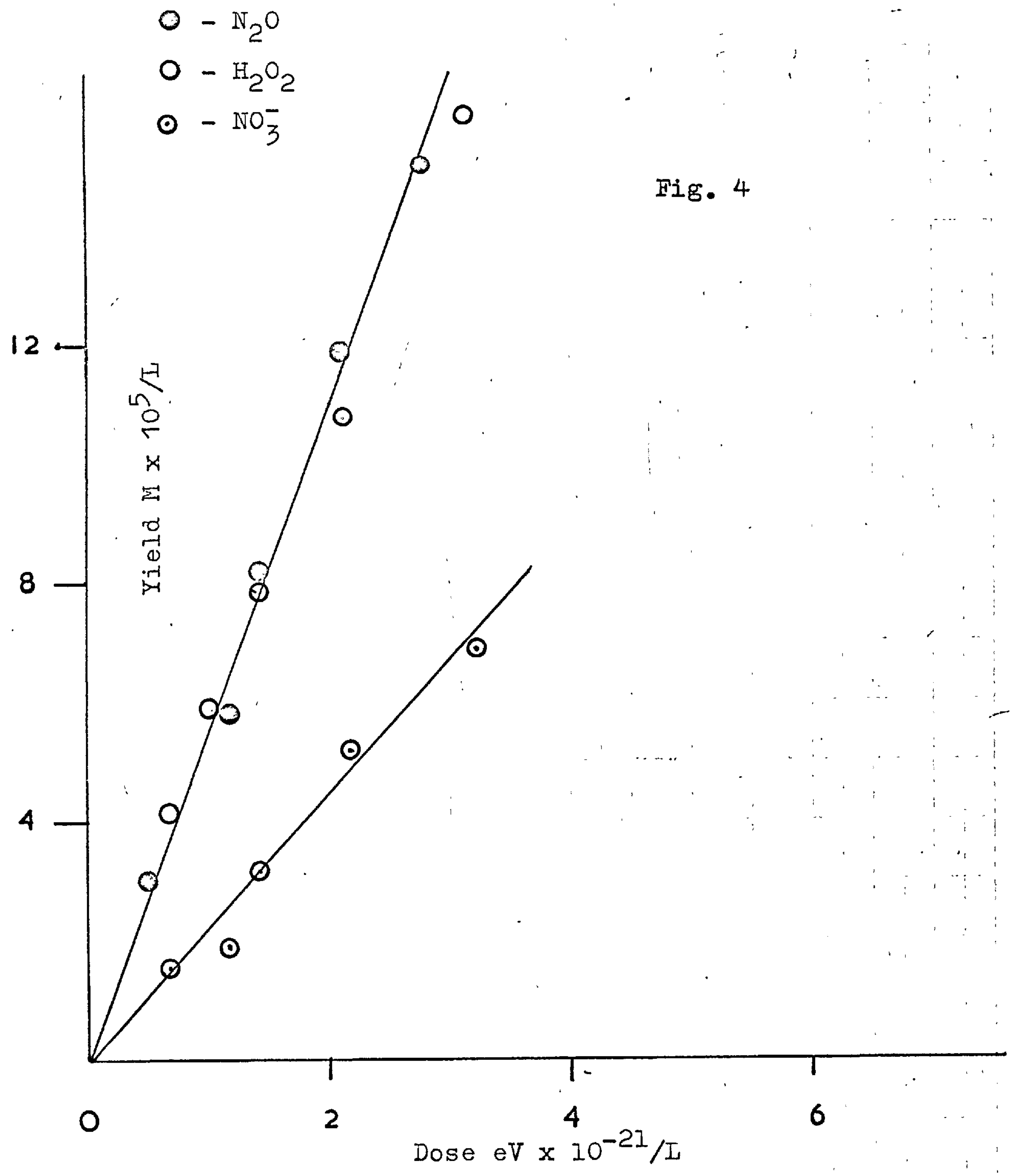


Fig. 4

γ-radiolysis of ethane-oxygen aqueous solutions.
Effect of added scavengers on hydrogen peroxide dose-yield curves.

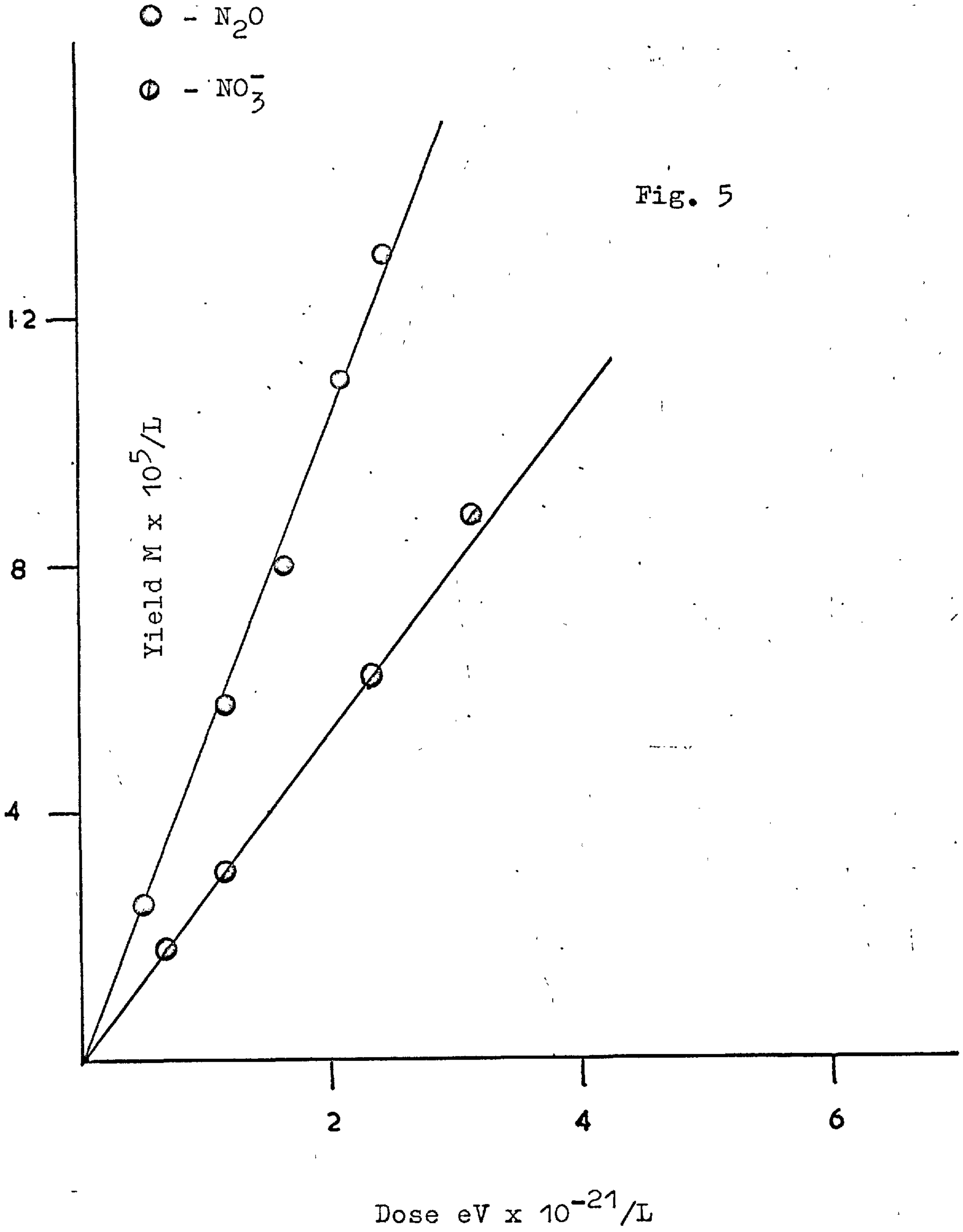


Fig. 5

of the irradiated solution was carried out, in part, to see if this was the explanation of the irreproducible yields. The effect of varying the temperature on the yields of the main products was investigated at both pH 1.2 and 5.5. The normal temperature of irradiation was about 20°C but some experiments were carried out at 28°C and 3°C; there appeared to be no significant effect of temperature on the radiation yields. At pH 1.2, the results were precisely the same at all three temperatures investigated. At pH 5.5, large variations in the yields of the products occurred at 3°C and 28°C, but there was no systematic change in the relative yields.

Increase in pH of the irradiated solutions from 5.5 to 10.0 decreased G($CH_3.CHO$) from 1.6 to 1.3 and G (H_2O_2) from 2.0 to 1.7. G ($CH_3.CH_2.OOH$) however, increased from 0.9 to 1.3. Further increase in pH, from 10.0 to 11.0, sharply decreased G ($CH_3.CHO$) from 1.3 to 0.6, and G (H_2O_2) from 1.7 to 0.9. G ($CH_3.CH_2OOH$) increased from 1.3 to 1.8 at the same time. It can be seen from table 1, that G (total organic products) in neutral and alkaline solutions is about 2.5, which is slightly higher than the accepted values of G_{OH} under these conditions.

Irradiations in the presence of dissolved electron scavengers.

The formation of organic hydroperoxides in irradiated aqueous solutions of organic compounds has been ascribed to the reactions of O_2^- ion with the alkyl peroxy radicals,

$$RO_2\cdot + O_2^- \longrightarrow RO_2^- + O_2 \qquad (1)$$

$$RO_2^- + H^+ \longrightarrow ROOH \qquad (2)$$

it should be possible to reduce G (ROOH) by the addition of electron scavenging solutes which suppress the formation of O_2^- ions. Nitrous oxide, hydrogen peroxide and nitrate ions were used as electron scavengers in the present work. The concentrations of nitrous oxide and hydrogen peroxide used were sufficient to scavenge about 98 %

and 75 % of the hydrated electron yield respectively. In both the electron scavenging systems, an irreproducible residual yield of ethyl hydroperoxide was observed(Appendix 1 A). Addition of nitrous oxide to the irradiated solution showed marked decrease in the yield of ethyl hydroperoxide at pH 5.5. The acetaldehyde and hydrogen peroxide yields increased at the same time but it can be seen from the Table 1, that the total measured yield of the organic products was less than the expected $G_{OH} + G_{e\ aq^-}$. Some ethanol was presumably formed but it was not measured.

Measurement of ethyl hydroperoxide in hydrogen peroxide electron scavenging was not very accurate however, fairly large residual yield of ethyl hydroperoxide, G = 0.6 was observed. This G-value is consistent with 75 % scavenging of $G_{e\ aq^-}$. Concentrations of hydrogen peroxide higher than those mentioned in Table 1 could not be used as under these conditions, the hydrogen peroxide competes with the ethane for hydroxyl radicals.

The addition of nitrate ions to the ethane-oxygen aqueous solutions did not apparently alter the yields of acetaldehyde, ethyl hydroperoxide and hydrogen peroxide as found in the irradiations at pH 5.5. However, it was apparent that some reaction with nitrate took place for $G(NO_2^-)$ = 1.2, was observed.

The effect of electron scavengers on the formation of ethyl hydroperoxide is not completely understood. A marked reduction in the yield of ethyl hydroperoxide is achieved by the addition of nitrous oxide but it is apparent that no simple conclusion can be drawn from the effect of added nitrate ions.

3.2. Photolysis of Dilute Hydrogen Peroxide Solutions In The Presence of Dissolved Ethane-Oxygen.

The photolysis of hydrogen peroxide solutions by light of wavelength 2537 A° is known to lead to the formation of OH radicals (Buxton and Wilmarth 1963). This provides a useful way of generating this species when it is wished to avoid complications due to electrons and hydrogen atoms. In the present experiments, hydrogen peroxide solutions (10^{-4} M) were photolysed in the presence of dissolved ethane-oxygen mixtures; $[C_2H_6] = 1.0 \times 10^{-3}$ M and $[O_2] = 7.0 \times 10^{-4}$ M. No ethyl hydroperoxide was formed under these conditions and ethanol and acetaldehyde were the only products detected. Photolysis of the solutions not containing hydrogen peroxide did not give any organic product; indicating the absence of chemical reactions due to direct absorption of light by ethane-oxygen system in aqueous solutions. Table 2 shows the results of photolysis experiments and it can be seen that acetaldehyde is a major product in both neutral and acidic solutions. Net decomposition of hydrogen peroxide was measured after each photolysis and it was found that this quantity is smaller than would be expected from the total amount of organic products formed. The average of acetaldehyde formed to hydrogen peroxide decomposed was approximately 4.8 in neutral solutions and 6.6 in acidic solutions. Ethanol is formed in smaller yields than those of acetaldehyde and its determination was not very accurate. On the average $[CH_3.CHO]/[CH_3.CH_2OH] = 5.69$ in neutral solutions and 8.13 in acidic solutions were observed.

<u>Reactivity of ethane towards OH radicals in aqueous solutions.</u>

It was necessary to establish that under the conditions of photolysis all the hydroxyl radicals produced by photochemical decomposition of hydrogen peroxide reacted with the ethane and not with the hydrogen peroxide. The relative reactivity of ethane towards hydroxyl radicals was determined by irradiating solutions pH 1.2, of ethane-oxygen; $[C_2H_6] = 1.0 \times 10^{-3}$ M and $[O_2] = 7.0 \times 10^{-4}$ M containing different concentrations of formic acid. The extent of the reaction of hydroxyl radicals with ethane was followed by the measurement of acetaldehyde formed. A good plot of $1 / G(CH_3.CHO)$ against $[HCOOH] / [C_2H_6]$ was obtained (Fig. 6), from which a value of $k_{OH + C_2H_6} / k_{OH + HCOOH} = 10$ may be derived. Since it is

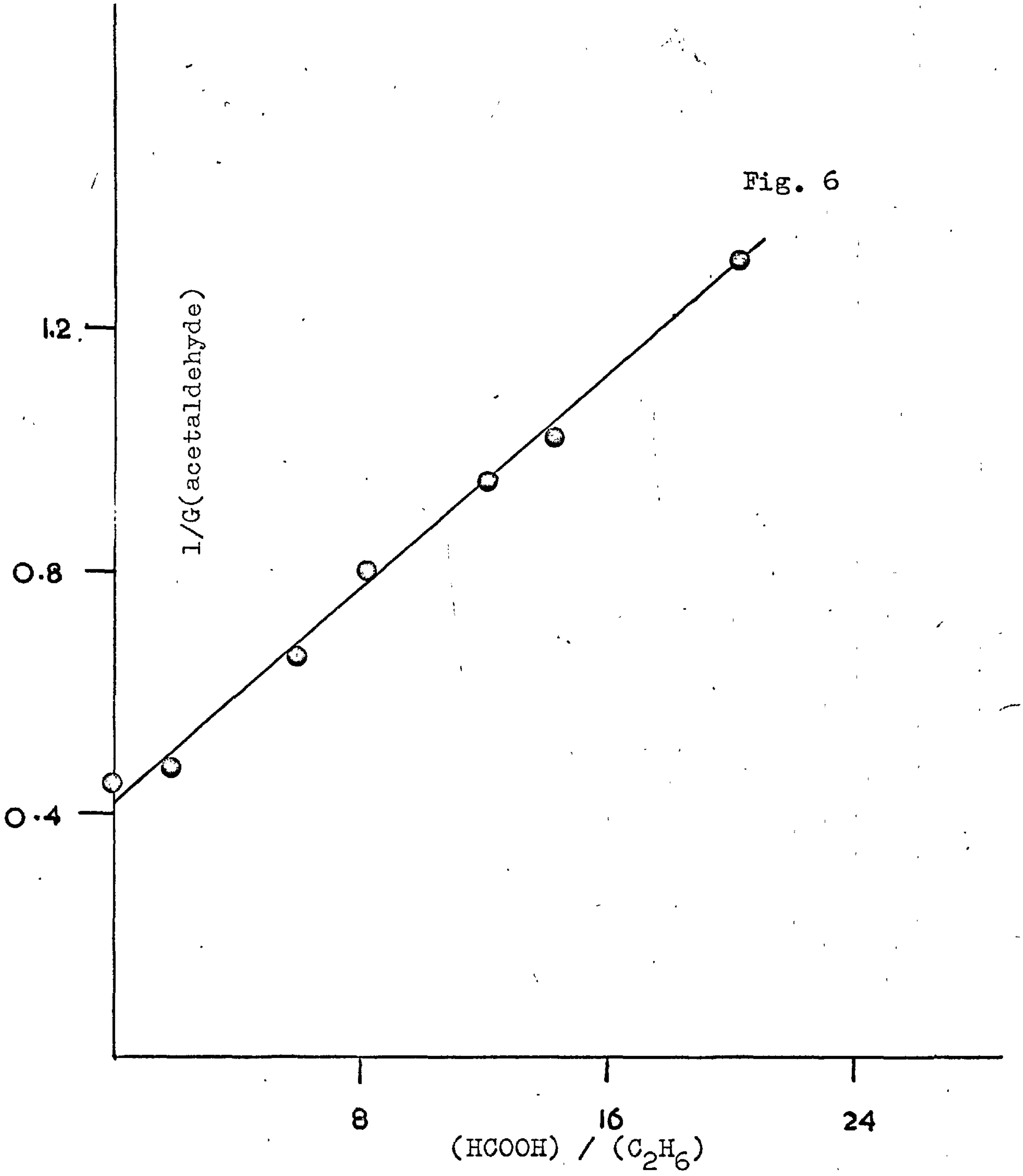
Photolysis of Ethane-Oxygen Aqueous Solutions.

Table 2.

	$M \times 10^4/L$			
pH	H_2O_2 (decomposed)	CH_3CHO	C_2H_5OH	$\frac{CH_3CHO}{H_2O_2 \text{ decom}}$
5.50	0.60	2.50	0.50	4.20
"	0.20	0.90	0.20	4.50
"	0.16	0.77	0.10	4.80
"	0.17	0.78	0.14	4.60
"	0.47	1.80	-	4.90
"	0.41	2.50	-	5.30
"	0.47	2.60	-	5.50
1.20	0.32	2.03	0.27	6.40
"	0.32	2.18	0.28	6.80
"	0.40	2.46	0.34	6.20
"	0.33	2.40	-	7.30
"	0.18	1.20	0.10	6.70
"	0.15	1.00	0.10	6.70
"	0.21	1.40	-	6.70
"	0.42	2.60	-	6.20
"	0.41	2.60	-	6.30

γ-radiolysis of ethane-oxygen aqueous solutions.
The effect of added formic acid on G(acetaldehyde).

Fig. 6



γ-radiolysis of ethane-oxygen aqueous solutions.

Effect of added hydrogen peroxide on G (acetaldehyde).

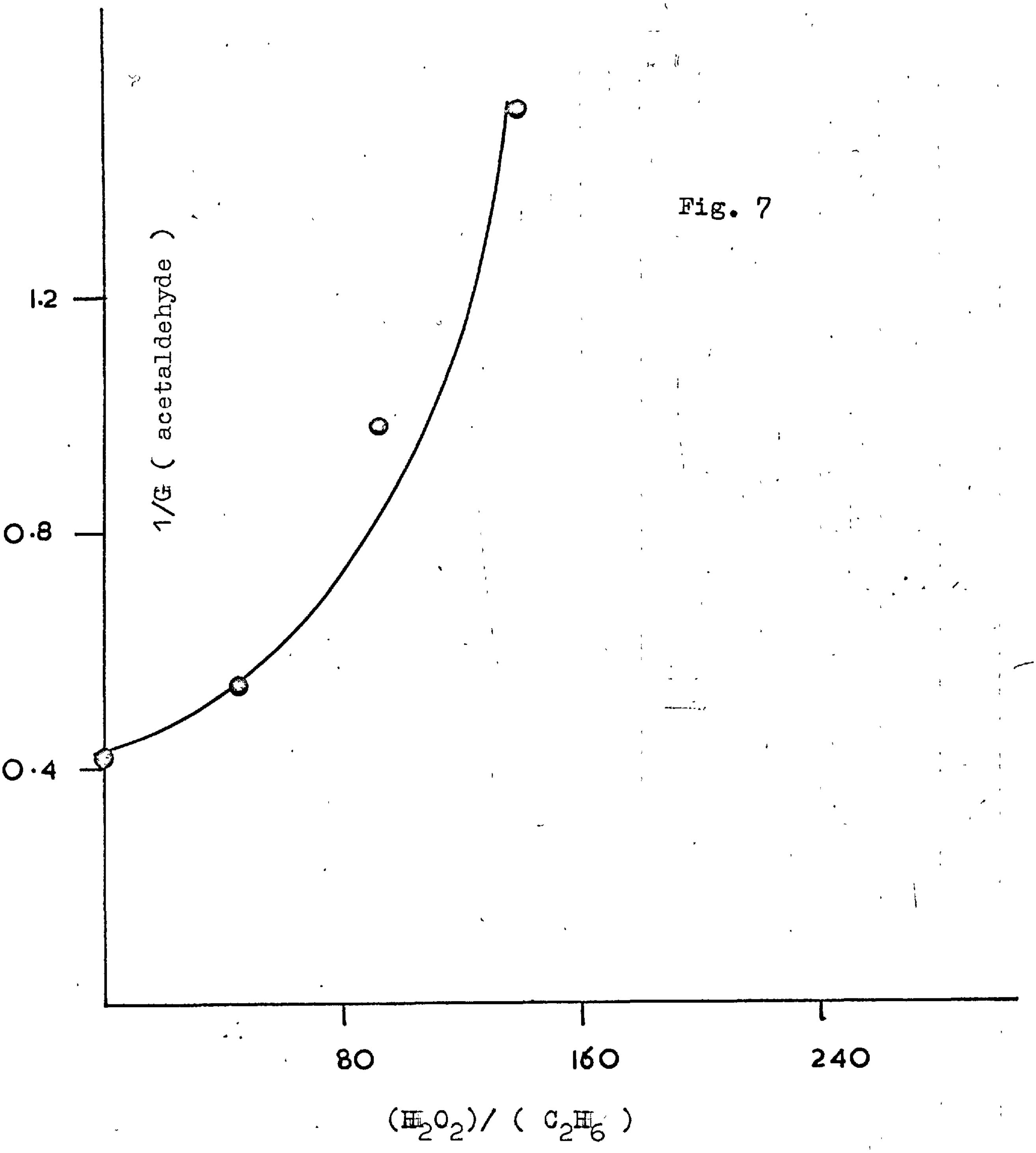


Fig. 7

γ-radiolysis of ethane oxygen aqueous solutions.

Effect of added chloride ions on G (acetaldehyde).

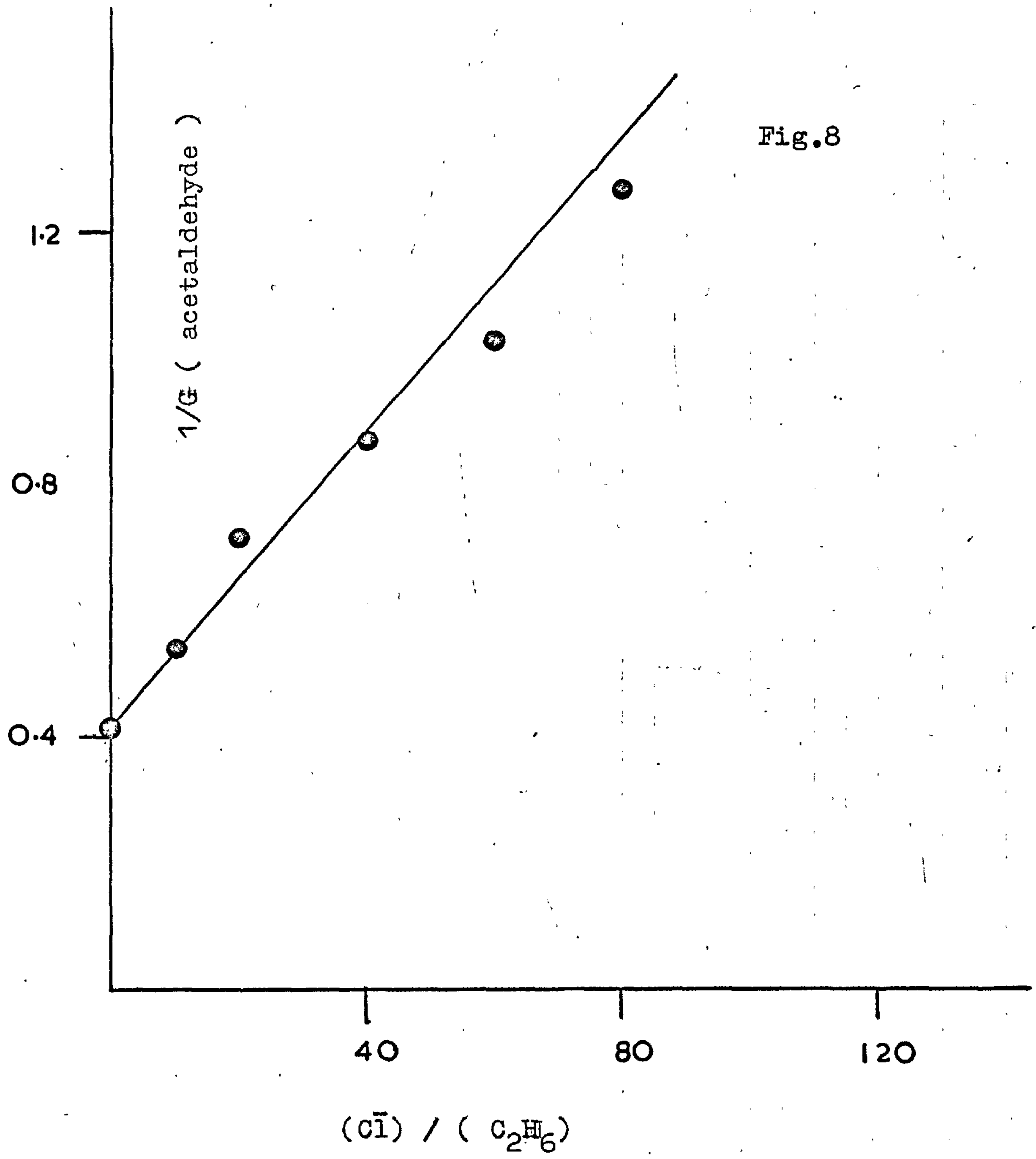


Fig.8

known that formic acid is some 10 times more reactive towards hydroxyl radicals than is hydrogen peroxide (Anbar and Neta 1965) it can be assumed that all the hydroxyl radicals produced in the photolysis experiments reacted with the ethane. Similar competition kinetic studies were made with hydrogen peroxide and chloride ions as the competitive hydroxyl radical scavengers. The plot of 1 / G ($CH_3.CHO$) against $[H_2O_2]/[C_2H_6]$ was not linear (Fig. 7) and required kinetic data could not be calculated with any degree of accuracy. An apparently good reciprocal plot (Fig. 8) was also obtained when chloride ions were used as scavenger. The results implied that ethane is approximately 10 times more reactive than chloride ions towards hydroxyl radicals at pH 1.2.

3.3. Radiolysis of Methane-Oxygen Aqueous Solutions.

Formaldehyde, formic acid, methanol, methyl hydroperoxide and hydrogen peroxide were the products detected in the radiolysis of methane-oxygen aqueous solutions, in qualitative agreement with the previous workers. Radiation yields of these products were studied as function of pH, methane-oxygen concentration and in the presence of electron and hydroxyl radical scavengers. G- values of the above mentioned products were calculated from the dose-yield **plots**. (Fig. 9 to 15) and also from the dose-yield tables given in the Appendices 2, 3, and 4. Preliminary experiments showed that in the radiolysis carried out at normal gas pressures ($[CH_4] = 2.0 \times 10^{-3}$ M and $[O_2] = 7.0 \times 10^{-4}$ M) the rates of the formation of formaldehyde and methyl hydroperoxide decreased at quite low total doses. Methyl hydroperoxide, being probably less prone to the attack of radicals, grew to relatively higher concentrations than formaldehyde. Hydrogen peroxide, which was the major product of the system, appeared to be least affected by the radical attack and dose-yield plots were linear up to a toal dose of 4.0×10^{21} eV L^{-1}. It can be seen from the

Radiolysis of Methane-Oxygen Aqueous Solutions.

Table 3: G values of the products.

Pressure of reactant gases : p.s.i.					G Values (molecules / 100 eV)					
pH	CH_4	O_2	H_2	N_2O	HCHO	CH_3OH	CH_3OOH	HCOOH	H_2O_2	G total organic produts
1.2	7.0	7.0	-	-	0.5±0.05	-	-	-	3.0±0.03	0.5±0.05
"	80.0	20.0	-	-	0.8±0.04	-	-	-	3.4±0.03	0.8±0.05
"	160	40.0	-	-	1.2±0.06	-	-	-	3.35±0.03	1.2±0.06
2.0	80.0	40.0	-	-	0.95±0.1	-	-	-	3.4±0.03	0.95±0.1
2.0	160	40.0	-	-	1.3±0.06	1.3±0.6	-	0.96±0.3	3.5±0.03	3.5±1.2
5.5	7.0	7.0	-	-	0.5±0.05	-	0.55±0.05	-	2.2±0.03	1.05±0.1
"	4.5	4.5	-	4.5	0.6±0.06	-	0.28±0.1	-	2.6±0.03	0.88±0.2
"	80.0	20.0	-	-	0.56±0.05	-	1.6±0.10	-	2.08±0.02	2.16±0.08
"	160	40.0	-	-	0.55±0.05	-	1.7±0.05	-	2.1±0.03	2.25±0.08
"	80.0	20.0	-	30.0	1.7±0.05	-	1.16±0.05	-	2.4±0.04	2.9±0.10
"	80.0	20.0	80.0	-	0.45±0.045	-	1.23±0.10	-	2.4±0.05	1.68±0.07

γ- radiolysis of methane-oxygen aqueous solutions.
Effect of methane concentration on formaldehyde dose-yield curves.
at pH 5.5

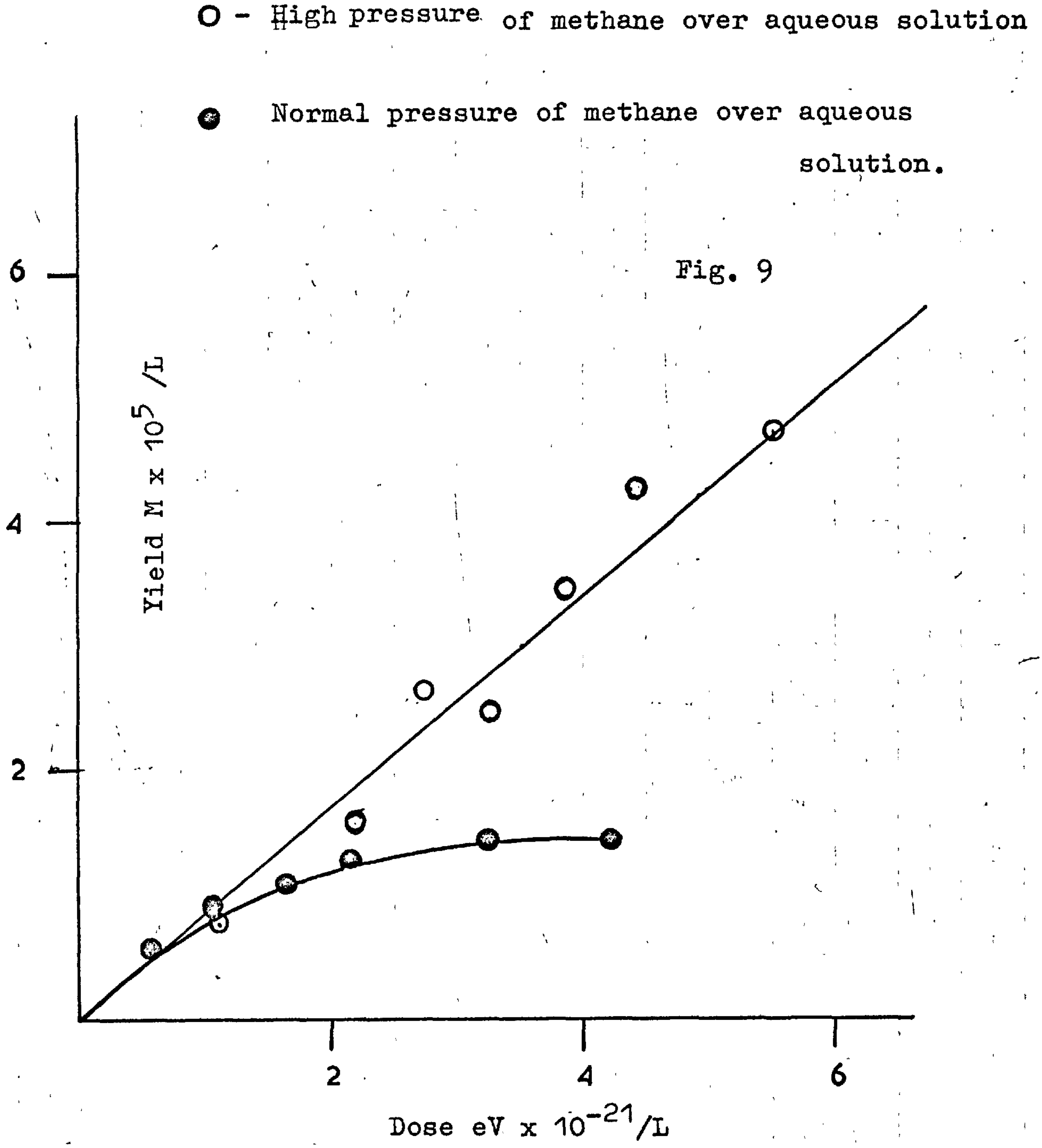


Fig. 9

γ- radiolysis of methane-oxygen aqueous solutions.
Effect of pH on formaldehyde dose-yield curves at
high methane oxygen pressure.

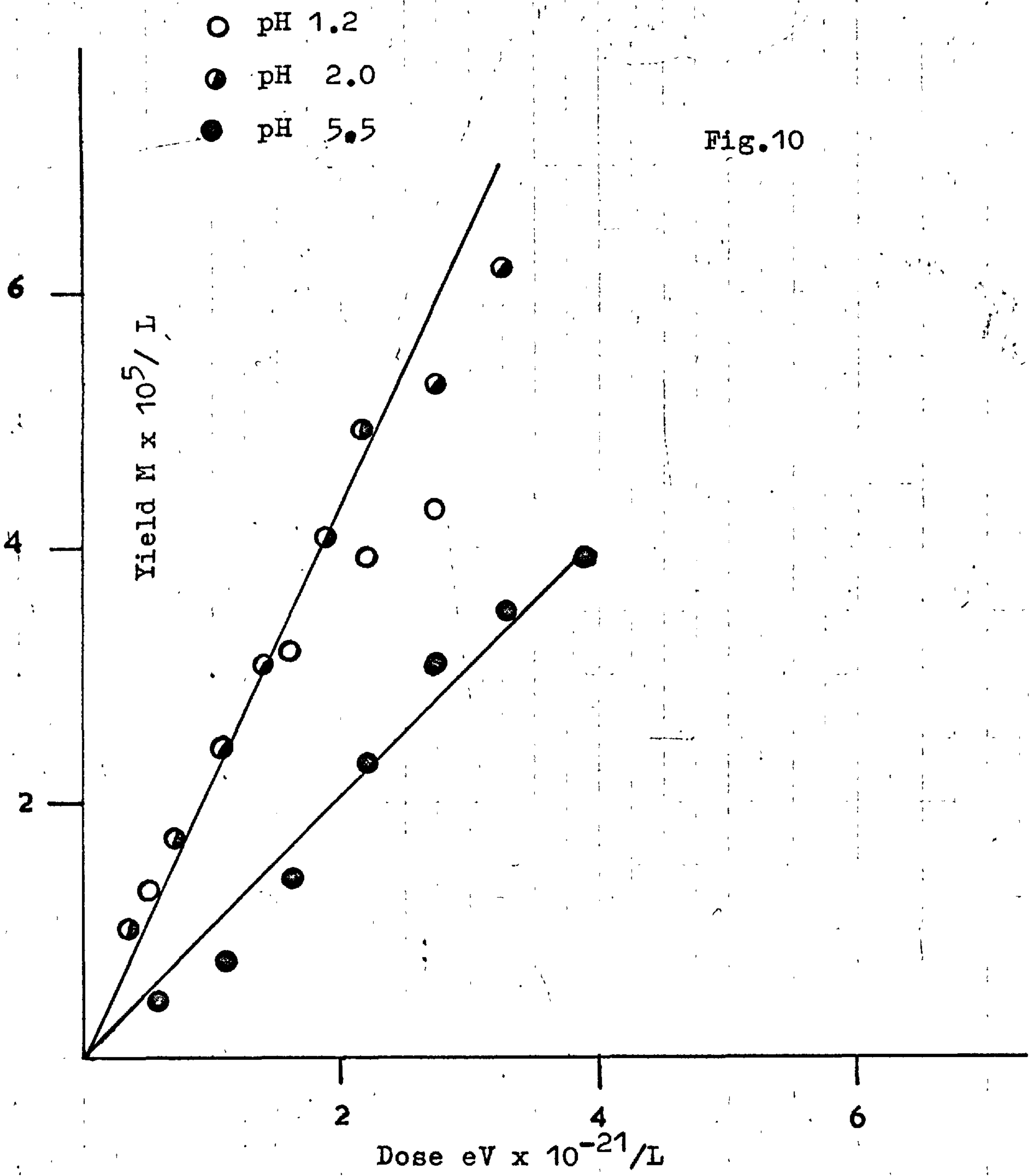


Fig.10

γ- radiolysis of methane-oxygen aqueous solutions.

Effect of methane concentration on formaldehyde dose - yield curves at pH 1.2

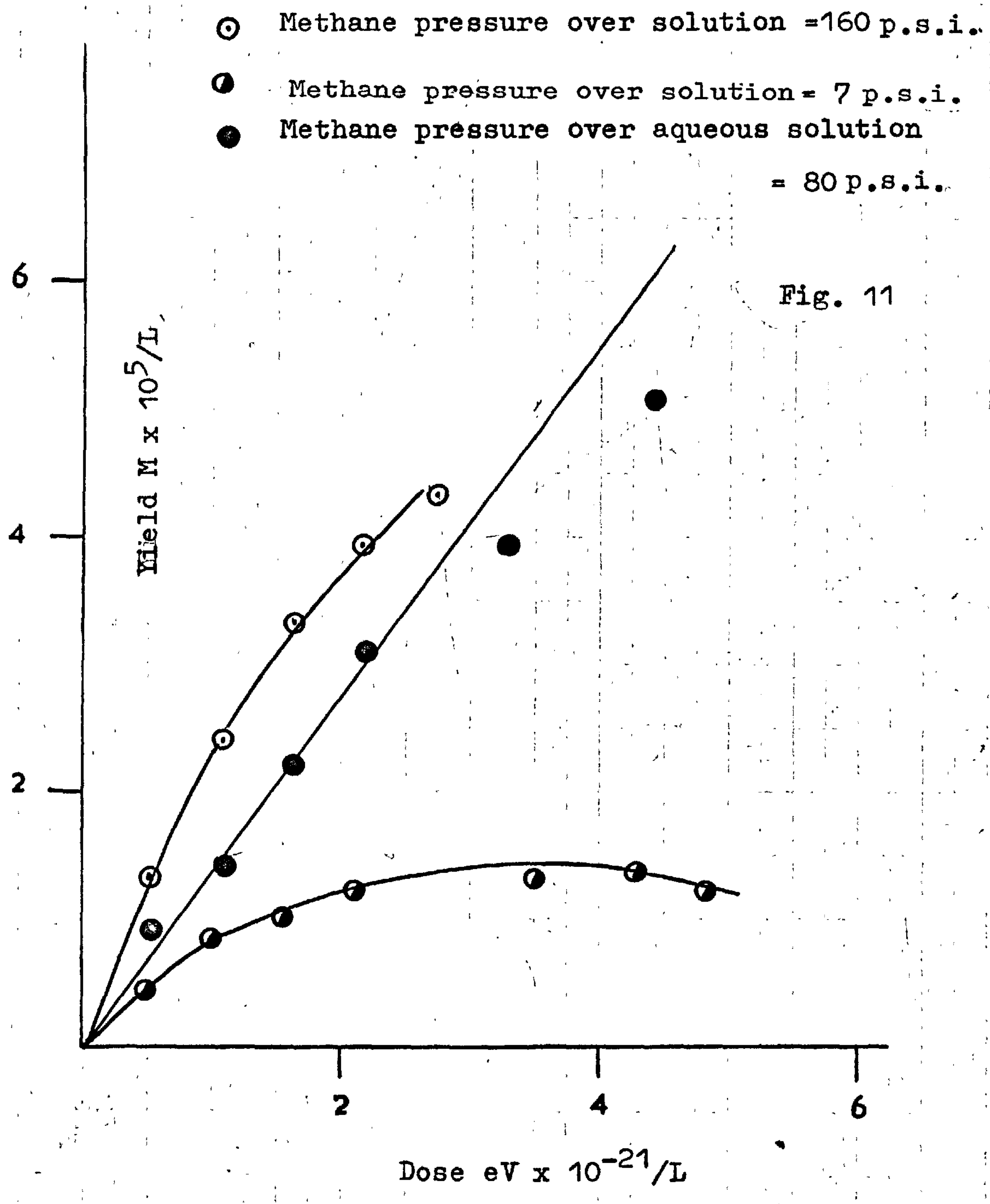
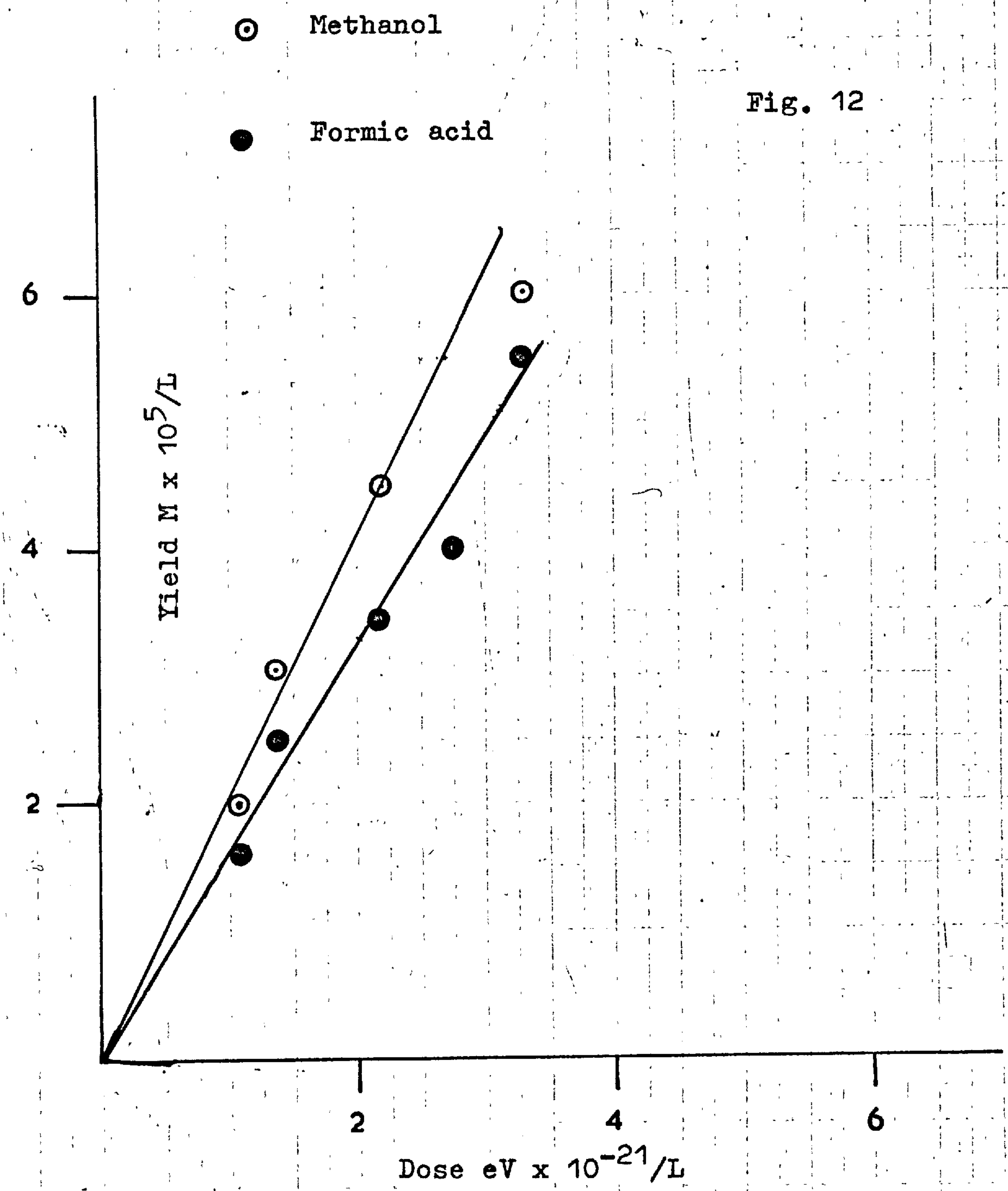


Fig. 11

γ- radiolysis of methane-oxygen aqueous solutions.

Methanol and formic acid dose-yield curves at pH 2.0

Fig. 12



γ-radiolysis of methane-oxygen aqueous solutions. Effect of methane concentration on the dose-yield curves of methyl hydroperoxide

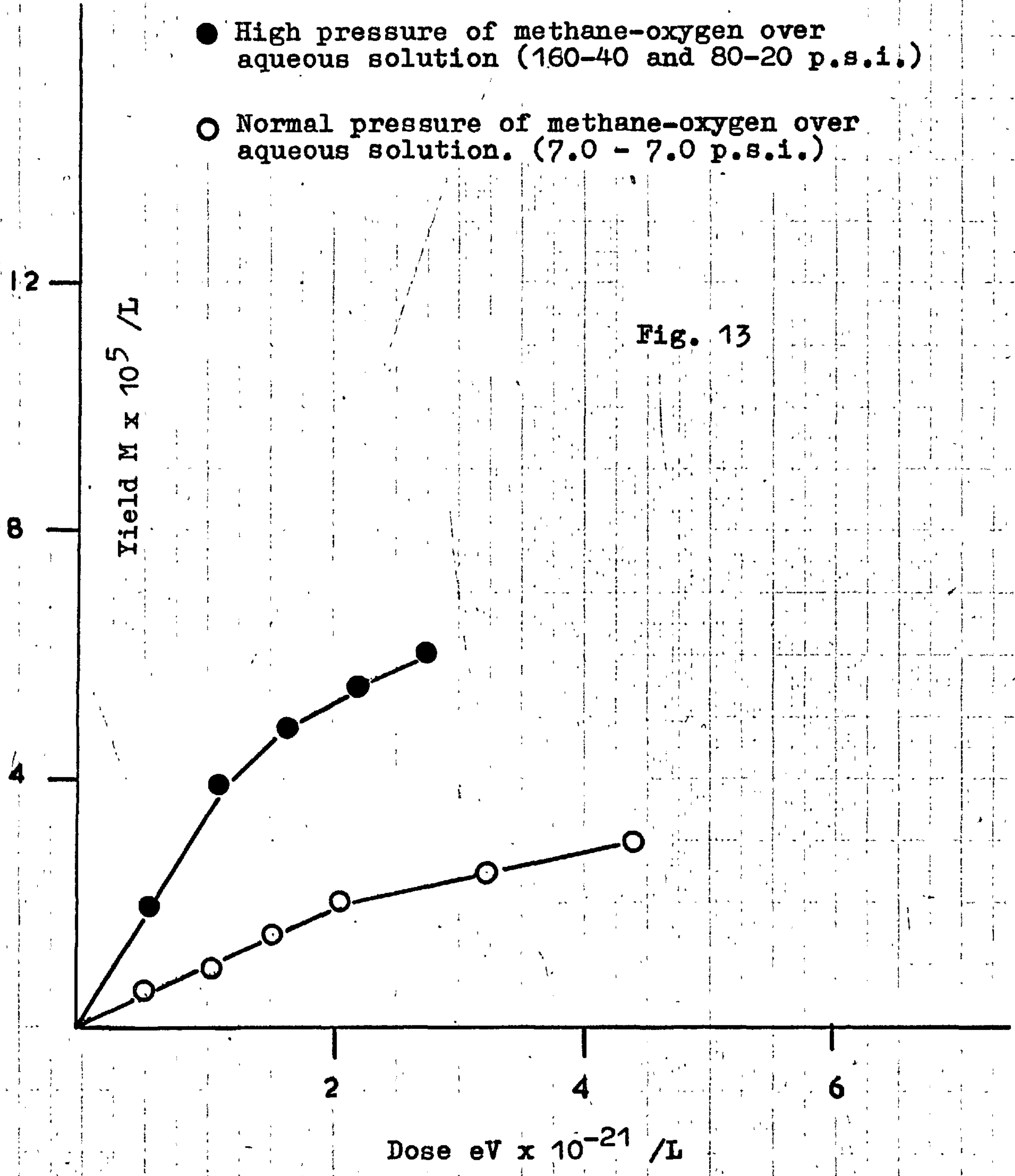


Fig. 13

γ- radiolysis of methane-oxygen aqueous solutions.

Effect of pH on hydrogen peroxide dose-yield curves.

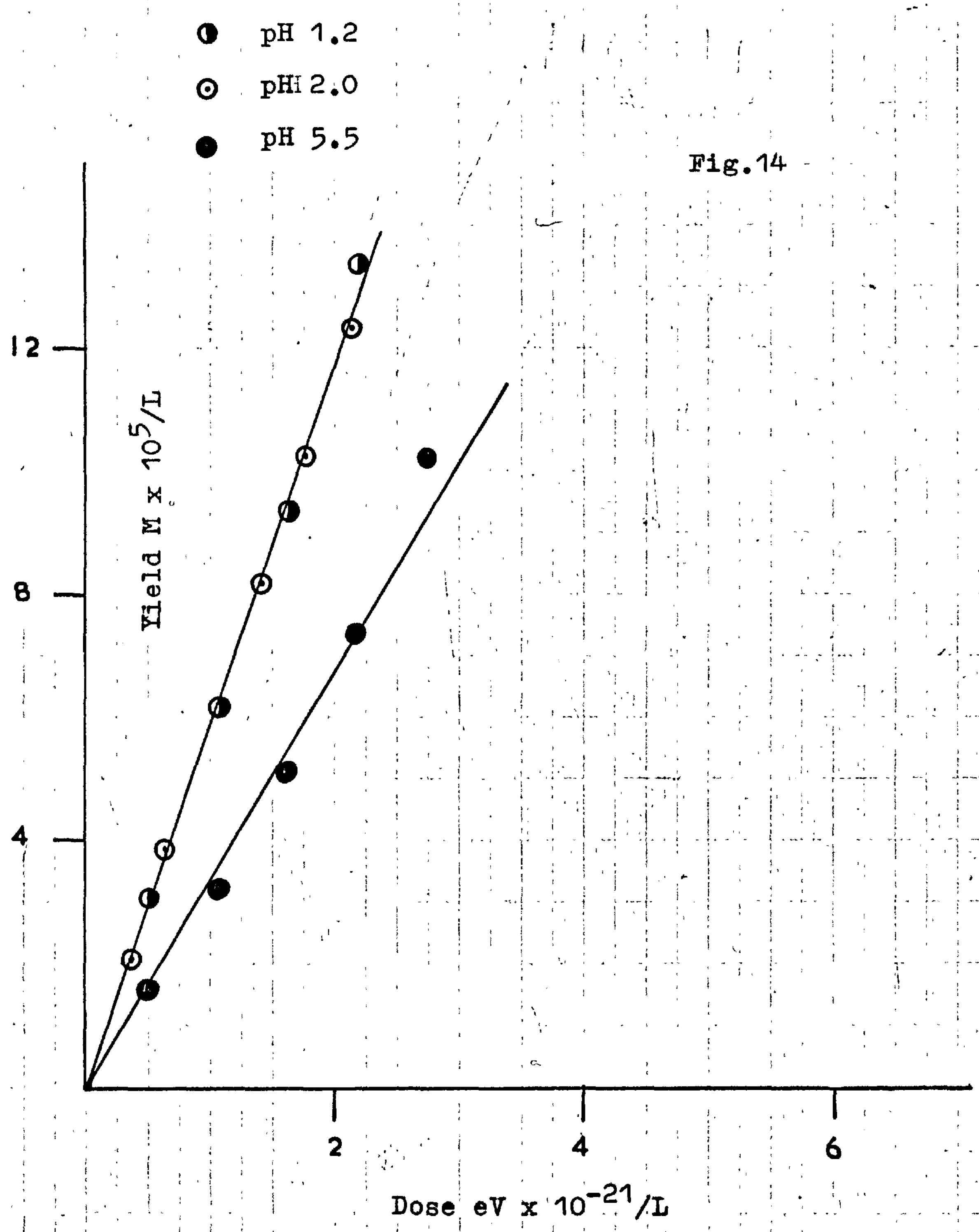


Fig.14

γ- radiolysis of methane-oxygen aqueous solutions. Effect of added nitrous oxide on methyl hydroperoxide dose-yield curves.

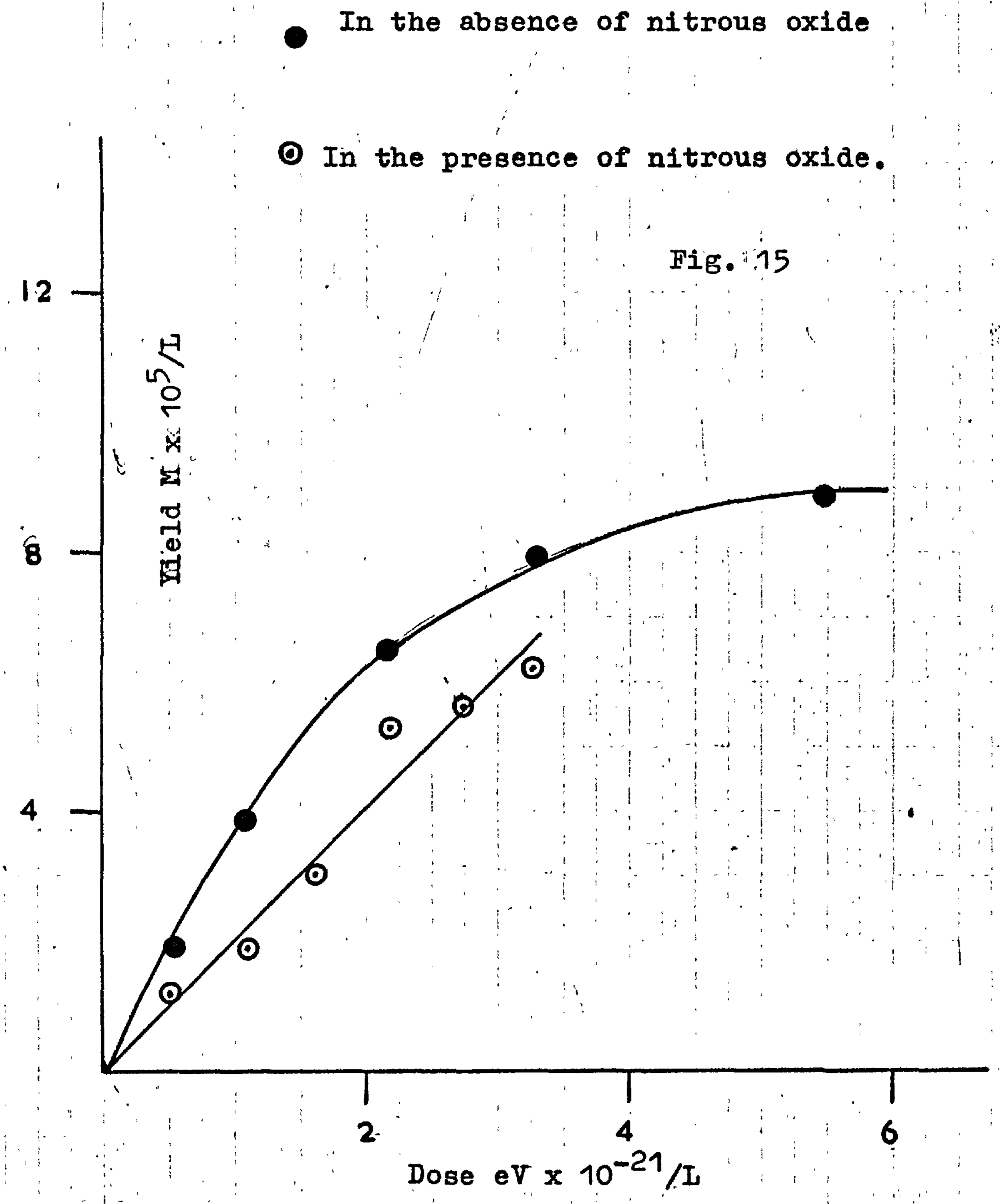


Fig. 15

Kinetics of organic hydroperoxides with iodide ions in aqueous solutions

Rate of increase of optical density (O.D.) of liberated iodine.

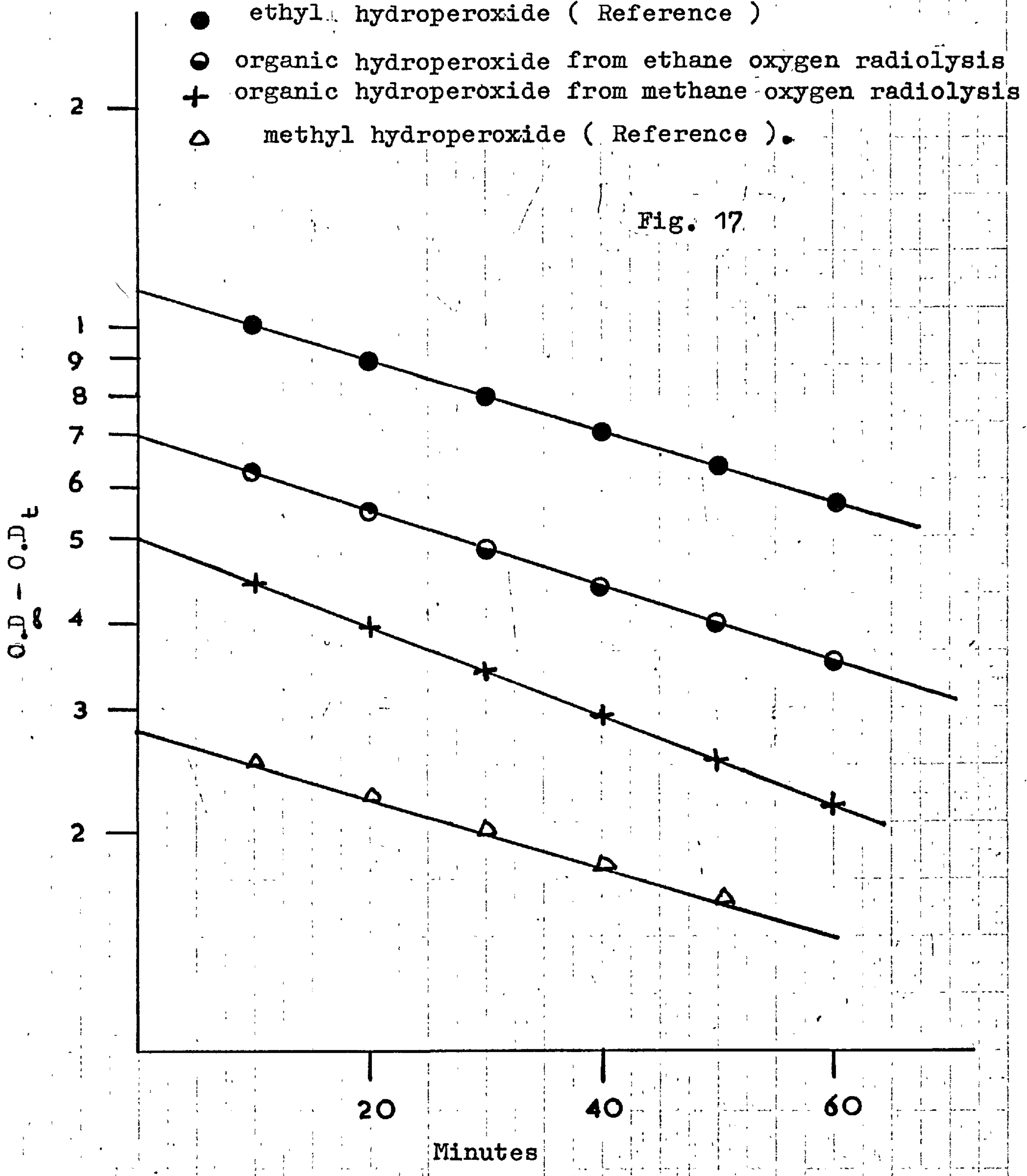
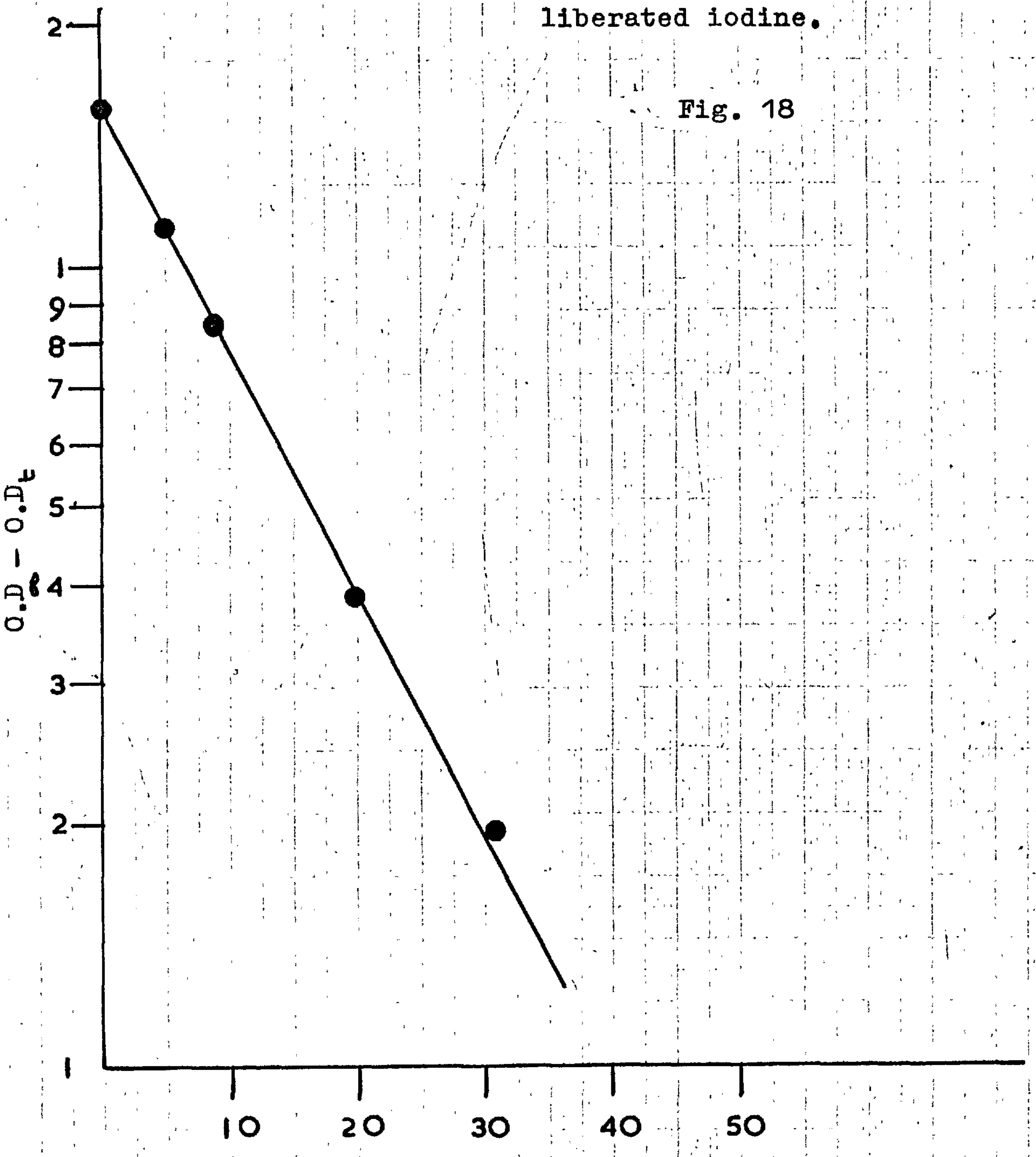


Fig. 17

Kinetics of hydroxy ethyl hydroperoxide with iodide ions in aqueous solutions.

Rate of increase of optical density (O. D) of liberated iodine.

Fig. 18



Minutes

Table 3 that formaldehyde and hydrogen peroxide were formed under all the conditions of radiolysis but formic acid and methanol were measured only in the high pressure radiolysis at pH 2.0 (Fig. 12). Methyl hydroperoxide was formed in neutral solutions only and its yield was found to be dependent on the concentration of solute gases.

Irradiations at pH 5.5.

Formaldehyde, methyl hydroperoxide and hydrogen peroxide were the only products detected at this pH. It can be seen from Table 3 that at normal pressure of solute gases, G (total organic products) = 1.05, which is considerably lower than G_{OH} at this pH. It seemed probable that this behaviour was a consequence of low reactivity of methane towards hydroxyl radicals and as a result of this, the competing concentrations of the products were rapidly reached. Subsequent experiments, carried out at higher methane-oxygen concentrations, showed that G (CH_3OOH) increased from 0.60 to 1.6. G (HCHO) = 0.55, was effectively the same at all the methane-oxygen concentrations investigated. It was also apparent that linearity of the formaldehyde dose-yield plots was maintained up to a total dose of 5.0×10^{21} eV L^{-1} (Fig. 9). A similar effect was observed at pH 1.2 and 2.0. At the higher methane-oxygen concentrations, at pH 5.5 radiolysis, G (total organic products) = 2.1 which approximates to G_{OH}. G (H_2O_2) = 2.1, was essentially the same at all the gas concentrations.

Irradiations at pH 1.2 and 2.0.

No methyl hydroperoxide was detected and formaldehyde and hydrogen peroxide were the only other products analysed for in solutions saturated at atmospheric pressure. G (total organic products) = 0.55, which was substantially lower than G_{OH} in acidic solutions . G (HCHO) increased with increasing pressure of methane- oxygen over aqueous solutions and for a given total pressure, was higher at pH2.0 than at pH 1.2 (Fig. 10 and 11). The increase in G (H_2O_2) was much smaller than formaldehyde in acidic solutions and varied from 3.0 and 3.5 between 7 p.s.i. g and 160 p.s.i. g. The experiments of Thomson showed that in solutions saturated at atmospheric pressure, the maximum product yield was encountered at pH 2.0 (clay). Table 3 shows that at elevated pressures of the solute gases, the yields of formaldehyde and hydrogen peroxide were similar to those at pH 1.2. Formic acid and methanol were also detected at pH 2.0 and it can be seen from (Fig. 12) that those were the primary products of radiolysis. The high G (total organic product) compared with G_{OH} at pH 2.0. could be due to the large errors showed in Table 3 in methanol determinations.

At pH 2.0, the effect of varying the concentration of oxygen at a constant methane concentration, on the yields of formaldehyde and hydrogen peroxide was also investigated. The results, recorded in the Appendix 4 showed that when pressure of oxygen over methane aqueous solutions was increased from 1.5 atm to 6.45 atm, there was no significant change in the G-values of formation of formaldehyde and hydrogen peroxide.

3.4. Photolysis of Hydrogen Peroxide Solutions Containing dissolved Methane-Oxygen.

Photolysis of methane-oxygen aqueous solutions at pH 1.2 and 5.5 gave formaldehyde and methanol as the main products. Neither formic acid nor methyl hydroperoxide were detected. The ratio $[HCHO]/[H_2O_2]$ (decomposed) depended upon hydrogen peroxide concentration before the photolysis and the amount of hydrogen peroxide decomposed, for a constant concentration of methane and oxygen in solution ($[CH_4] = 2.0 \times 10^{-3}$ M and $[O_2] = 7.0 \times 10^{-4}$ M). It can be seen from the Table 4 that at high initial hydrogen peroxide concentration and at high % decomposition, this ratio was decreased. It was found that the decomposition of one molecule of hydrogen peroxide

Photolysis of Methane-Oxygen Aqueous Solutions.

Table 4 .

$M \times 10^5/L$

pH	Initial H_2O_2	H_2O_2 decomp	HCHO	CH_3OH	$HCHO/H_2O_2$ dec
5.5	15.00	5.25	3.40	3.70	0.60
	15.00	10.60	4.50	3.70	0.42
	2.60	1.39	2.00	-	1.44
	2.60	0.38	0.60	-	1.58
	2.70	0.61	1.40	-	2.30
	3.40	0.17	0.30	-	1.72
	3.40	0.52	0.60	-	1.15
	3.40	0.78	0.85	-	1.08
	3.40	1.03	1.10	-	1.07
	9.75	0.87	1.15	-	1.32
	9.75	1.30	1.60	-	1.23
	9.75	1.90	1.90	-	1.00
	10.00	3.15	1.80	-	0.64
	157.00	97.00	2.10	-	0.021
1.20	10.00	1.91	1.30	-	0.690
	10.00	1.39	0.80	-	0.575
	10.00	2.40	1.60	-	0.665

into hydroxyl radicals resulted in the formation of at the most two molecules of formaldehyde. Methanol measurements were qualitative and were carried out in a limited number of experiments. From the figures mentioned in the Table 4 it would appear that methanol yields were of the same order as those of formaldehyde . Little quantitative information can be extracted from these results because of the competition between the products and methane for hydroxyl radicals.

Reactivity of methane towards hydroxyl radicals.

It was desirable to obtain an estimate of the rate constant for the reaction between methane and hydroxyl radicals in aqueous solutions.

$$OH + CH_4 \xrightarrow{k_3} CH_3\cdot + H_2O \qquad (3)$$

In the case of radiolysis, the formation of formaldehyde was studied as a function of dose at pH 5.5 and at atmospheric pressures. Under these conditions formaldehyde concentration grows to a maximum of 1.4×10^{-5} M (Fig. 9). Increase in the dose did not increase the formaldehyde yield and presumably at this point the rate of formation of formaldehyde is equal to its rate of destruction by the hydroxyl radicals.

$$OH + HCHO \xrightarrow{k_4} \text{Secondary products.} \qquad (4)$$

From reactions (3) and (4):

$$k_3 \left[CH_4\right] = k_4 \left[HCHO\right]$$

k_4 in aqueous solutions and at room temperatures is known to be about 2.0×10^9 M^{-1} sec^{-1} and substituting this value and those of methane and formaldehyde concentrations in the above equation $k_3 = 1.4 \times 10^7$ M^{-1} sec^{-1}.

Methane-oxygen aqueous solutions containing different concentrations of formaldehyde were photolysed and the decomposition of hydrogen peroxide and net formation of formaldehyde were measured at the end of each experiment. It was found that at low concentrations of added formaldehyde there was a net formation of formaldehyde but at higher concentrations, there was a net decomposition. The difference of these quantities before and after photolysis was plotted against the initial formaldehyde concentration. From the plot (Fig. 16) it was deduced that for a constant concentration of $[CH_4] = 2.0 \times 10^{-2}$ M, $[O_2] = 7.0 \times 10^{-4}$ M and $[H_2O_2] = 1.0 \times 10^{-4}$ M the competing concentration of formaldehyde (reactions 3 and 4) is 1.28×10^{-5} M. This value on substitution in the equation yields $k_3 = 1.28 \times 10^{7}\ M^{-1}\ sec^{-1}$, which is essentially the same as found from the radiolysis experiments.

The rate constant k_3 determined above appears to be similar to the rate constant of the reaction between hydrogen and hydroxyl radicals in aqueous solutions (Allen and Schwarz 1959) and (Schwarz 1962). This provided a method for checking the value of k_3 estimated in the present work. A solution containig $[CH_4] = 2.5 \times 10^{-2}$ M, $[O_2] = 2.0 \times 10^{-3}$ M and $[H_2] = 5.3 \times 10^{-3}$ M was subjected to radiolysis. The results listed in Table 3 show a marked decrease in G (total organic products) which has fallen from 2.16 in solutions not containing hydrogen to 1.68 in solutions containing dissolved hydrogen. If it is assumed that this 20 % reduction in the yield of organic products is due to the competition of reactions (3) and (5) then the same value should be obtained by the consideration of the reactivities of hydrogen and methane in aqueous solutions.

$$OH + H_2 \longrightarrow H + H_2O \qquad (5)$$

$$OH + CH_4 \longrightarrow CH_3\cdot + H_2O \qquad (3)$$

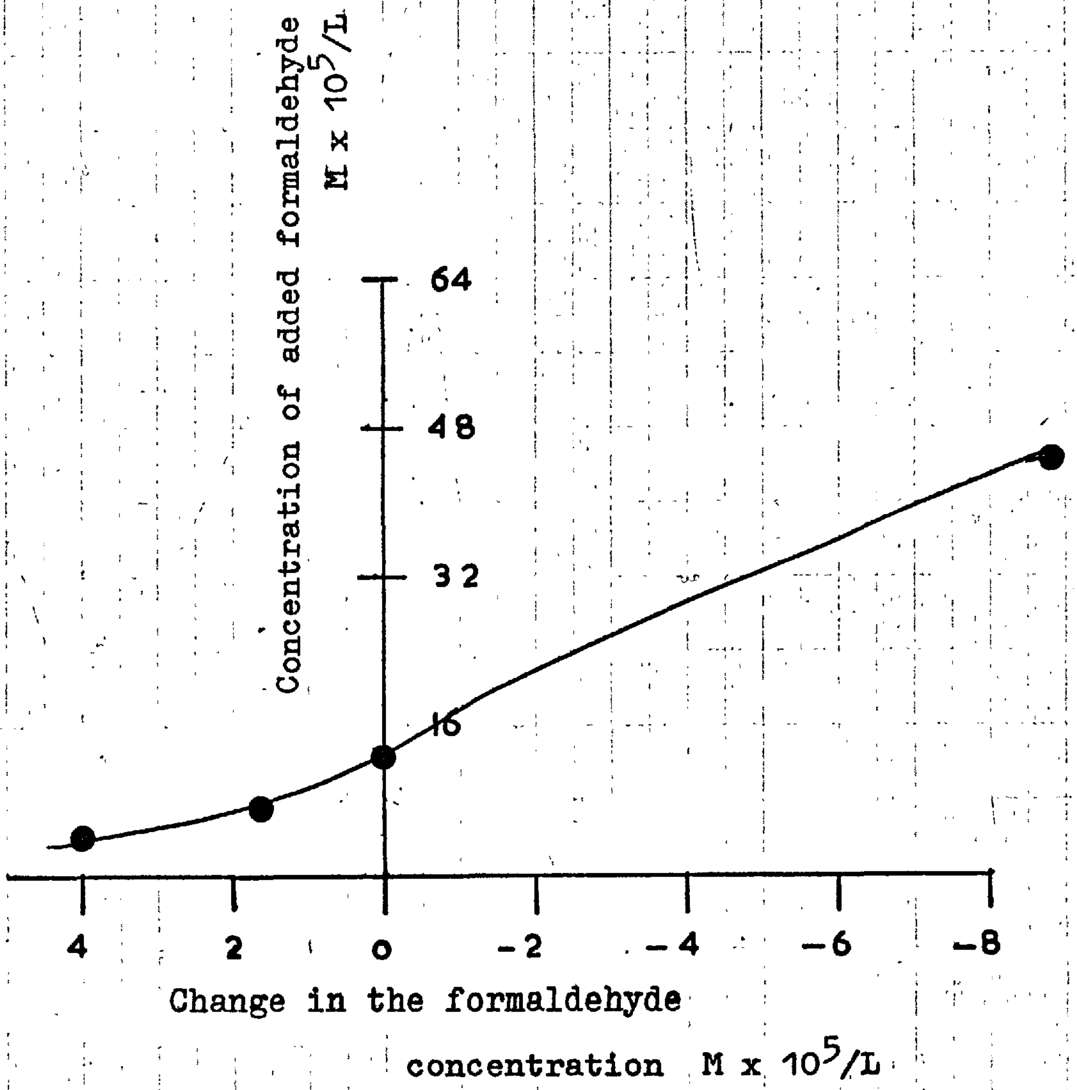
The relative rate of reaction of hydroxyl radicals with hydrogen and methane will be given by $k_5[H_2]$ / $k_3[CH_4]$ steady state. Therefore,

$$\frac{k_3[CH_4]}{k_3[CH_4] + k_5[H_2]} = \frac{1.68}{2.16}$$

Photolysis of methane-oxygen aqueous solutions.

Effect of added formaldehyde on the formation of formaldehyde.

Fig. 16



From which,

$$k_3 = \frac{0.777 \times k_5 [H_2]}{1 - 0.777 \times [CH_4]}$$

substituting $k_5 = 4.5 \times 10^7\ M^{-1}\ sec^{-1}$,
$k_3 = 3.2 \times 10^7\ M^{-1}\ sec^{-1}$. at 20^0 C.

The value of k_3 derived in this way is about twice as much the value obtained by formaldehyde competition method but nevertheless, is of the right order. More accurate methods are needed to determine k_3 in aqueous solutions . Pulse radiolysis of aqueous solutions of methane could be a useful technique to achieve this end.

Irradiation of methane-oxygen aqueous solutions in the presence of dissolved nitrous oxide.

Nitrous oxide is a specific scavenger for the hydrated electrons in aqueous solutions. In methane-oxygen system, this scavenger was used at both normal and high pressures of solute gases. It can be seen from Table 3 that in solutions saturated with CH_4 = 4.5 p.s.i. g, O_2 = 4.5 p.s.i. g and N_2O = 4.5 p.s.i. g, no significant change in the G-values of organic products occurred. G (total organic products) = 0.88 was much smaller than $G_{OH} + G_{e\ aq^-}$. The value of latter quantity could be as high as 5.0. As mentioned before, since formaldehyde starts competing with methane for hydroxyl radicals even at low total doses, the representative G-values for various products formed in this system may be misleading. In order to gain a better understanding of the nature of the radiolysis in the presence of nitrous oxide, the concentration of the reactant gases in solution was increased to $[CH_4] = 1.0 \times 10^{-2}$ M, $[O_2] = 2.0 \times 10^{-3}$ M and $[N_2O] = 5.0 \times 10^{-2}$ M. The concentration of nitrous oxide used was enough to scavenge 90 % of electron yield and under these conditions, radiolysis of the solutions gave G (HCHO) = 1.7, G (CH_3OOH) = 1.15 and G (H_2O_2) = 2.4. The observed G (total organic product) = 2.85, although higher than that observed at atmospheric pressure, was still considerably smaller than G_{OH} + $G_{e\ aq^-}$. Some methanol was presumably formed but it was not measured because of the interference by methyl hydroperoxide.

3.5. Photolysis of Hydrogen Peroxide Solutions Containing dissolved Ethylene-Oxygen.

The photolysis technique of generating OH radicals from the decomposition of hydrogen peroxide was found to be very satisfactory for both ethane-oxygen and methane-oxygen systems. The hydroxyl radicals produced in this way are efficiently scavenged by the dissolved hydrocarbons. In the case of methane and ethane, the only reaction of this species is the dehydrogenation of the organic solute but in ethylene aqueous solutions, addition of hydroxyl radicals to the unsaturated bond is also probable.

The solution for photolysis contained $[C_2H_4] = 3.7 \times 10^{-3}$ M $[O_2] = 1.0 \times 10^{-3}$ M and $[H_2O_2] \sim 10^4$ M. Formaldehyde, formic acid hydroxyethanal and an organic hydroperoxide were the products detected in the photolysed solutions. Chromatography of the 2:4 dinitro phenyl hydrazones demonstrated that acetaldehyde was not a product under these conditions. This was also confirmed by the gas chromatography of the photolysed solutions by the technique described for ethanol determination. No attempt was made to analyse the photolysed solutions for glycol, which is very probably formed in this system. Neither glycol nor formic acid was measured in the radiolysis of ethylene-oxygen aqueous solutions in the previous studies. When the photolysis was carried out with the filtered light in the absence of dissolved hydrogen peroxide, no organic products were detected; indicating the absence of chemical reactions by direct absorption of 2537 A° light.

Kinetic studies on the organic peroxide showed that it reacted with the iodide reagent much faster than methyl or ethyl hydroperoxide (Fig. 17 and 18). A value of the rate constant for pseudo first order reaction = 1.28 x 10^{-4} sec^{-1} was derived from the slope of the curve (Fig. 18). This value was little affected by the ammonium molybdate catalyst, and was in agreement with that obtained by Francis under identical conditions (Francis 1963). He also synthesised the expected hydroxy ethyl hydroperoxide and the values of the rate constant for synthetic and unknown organic peroxide were 1.28 x 10^{-4} sec^{-1} and 1.36 x 10^{-4} sec^{-1}, respectively. From this comparison, the formation of hydroxy ethyl hydroperoxide was concluded and no further characterization was attempted in this work.

Photolysis was carried out in both neutral and acidic solutions and it can be seen from Table 5 that the major products, formaldehyde and hydroxyethanal, were formed in 1:1 ratio. The formic acid yield was pH dependent; being lower in acidic solutions than in neutral solutions. Hydroxy ethyl hydroperoxide was formed under all conditions of photolysis and its rate of formation was independent of pH. It was observed to grow only to relatively small concentrations and unlike other products, came to a plateau concentration . Net decomposition of hydrogen peroxide was measured after each photolysis and the ratios of the yields of various products to this quantity were evaluated from the figures given in Table 5.

	$\frac{[HO.CH_2.CHO]}{[H_2O_2]}$	$\frac{[HCHO]}{[H_2O_2]}$	$\frac{[HCOOH]}{[H_2O_2]}$	$\frac{[HO.CH_2.CH_2OOH]}{[H_2O_2]}$
<u>pH 5.5</u>				
	1.43	1.28	0.88	0.42

Photolysis of Ethylene-Oxygen Aqueous Solutions.

Table 5 .

$M \times 10^5/L$

pH	Initial H_2O_2	H_2O_2 decomposed	$HO.CH_2.CHO$	HCHO	$HO.CH_2.CH_2.OOH$	HCOOH
5.5	17.89	8.95	12.80	11.50	3.76	7.95
	18.30	8.17	12.50	12.10	4.23	6.40
	19.00	12.0	16.77	16.50	4.55	–
	17.30	10.30	14.40	13.20	4.30	6.17
	17.45	12.00	14.50	24.00	5.35	4.85
	16.80	11.65	16.30	20.10	4.85	8.85
	25.70	14.50	19.20	18.40	6.00	9.30
	26.08	14.65	20.40	23.00	4.22	9.30
	24.90	17.20	19.50	24.00	1.95	14.50
	24.90	14.70	19.80	20.00	5.45	9.70
2.0	18.80	9.96	17.90	17.40	3.34	1.77
	19.00	10.10	21.30	21.20	2.10	4.80
	18.90	10.05	19.30	19.30	3.05	2.66

1.51	1.48	0.78	0.52	
1.39	1.37	0.41	0.37	
1.20	1.28	0.77	0.40	
1.39	2.00	0.64	0.43	
1.38	1.49	0.70	0.43	Average values
pH 2.0				
1.79	1.74	0.18	0.34	
2.00	2.00	0.48	0.21	
1.83	1.83	0.25	0.30	
1.87	1.82	0.30	0.28	

It can be seen that the measured decomposition of each molecule of hydrogen peroxide leads to the formation of 2.82 and 3.36 molecules of organic products (counting the yields of formaldehyde and formic acid together; the yields of the precursors of these products = $\frac{1}{2}$ (HCOOH + HCHO). However, the actual amount of hydrogen peroxide decomposed required for the observed products formation is given by:

$$: \cdot OH = (HO.CH_2.CHO + HO.CH_2.CH_2OOH) + \frac{1}{2}(HCHO + HCOOH)$$

and the total observed organic product yield is thus a measure of the hydrogen peroxide actually decomposed by the light into hydroxyl radicals. That the ratio [organic produt]/ 2 to observed [hydrogen peroxide] decomposed greater than unity(1.41 and 1.68 at pH 5 & 2) indicated that hydrogen peroxide was a product of the reactions following that of hydroxyl radicals with ethylene. The extent of initial hydrogen peroxide decomposition was determined by measuring the decomposition of hydrogen peroxide in the presence of allyl alcohol in deaerated aqueous solutions. Under these conditions, the hydroxyl radicals react quantitatively with ally alcohol without reforming hydrogen peroxide (Volman and Chan 1959). The results of these irradiations (Appendices 9 and 10) showed that approximately, the rate of destrucion of hydrogen peroxide in allyl alcohol divided by this quantity, at a given initial hydrogen peroxide concentration, in ethylene-oxygen aqueous solutions = 1.28 and 1.71 at pH 5.5 and 2.0 respectively (Appendix 10). This can be compared with the rate of destrucion of hydrogen peroxide calculated from the product yields:

pH 5.5	pH 2.0	
1.47	1.62	
1.37	1.80	
1.42	1.73	
1.52	1.59	
1.34	-	
1.42	1.68	Average.

It can be seen that there is a fairly good agreement between the observed and calculated values.

The effect of changing the concentration of solute gases on the yields of the products per molecule of hydrogen peroxide apparently decomposed was investigated and the results are recorded in Table 6. It can be seen that at $[C_2H_4] = 6.7 \times 10^{-3}$ M and $[O_2] = 4.0 \times 10^{-4}$ M, the yields of the observed organic products for a

Table 6

Photolysis of Ethylene-Oxygen Aqueous Solutions.

Effect of ethylene and oxygen concentration on the product yield .

$[C_2H_4] = 6.7 \times 10^{-3}$M $[O_2] = 4 \times 10^{-4}$ M

M x 10^5/L

Initial H_2O_2	H_2O_2 decomposed	$HO.CH_2.CH_2OOH$	HCHO	$HO.CH_2.CHO$
16.34	8.17	2.33	8.70	9.75
21.60	12.70	2.90	12.00	9.75
21.60	12.20	3.60	12.50	11.50
21.60	14.25	3.05	12.00	12.00

$[C_2H_4] = 1.85 \times 10^{-3}$ M $[O_2] = 1.4 \times 10^{-3}$ M

19.00	8.40	4.10	15.80	11.90
19.50	8.50	4.00	13.00	13.00
19.50	9.10	3.60	21.00	13.80
19.50	9.00	3.50	23.00	13.50
19.30	9.05	4.65	20.00	12.80

given amount of hydrogen peroxide decomposed is smaller than those calculated from Table 5.

pH 5.5

$\frac{[HOCH_2.CHO]}{[H_2O_2]}$	$\frac{[HCHO]}{[H_2O_2]}$	$\frac{[HO.CH_2.CH_2OOH]}{[H_2O_2]}$
1.19	1.06	0.28
0.77	0.94	0.23
0.95	1.00	0.30
0.48	0.84	0.21
0.85	0.96	0.254

$[C_2H_4] = 1.85 \times 10^{-3}$ M and $[O_2] = 1.4 \times 10^{-3}$ M.

1.42	1.88	0.50
1.52	1.52	0.50
1.51	2.38	0.40
1.50	2.55	0.40
1.42	2.20	0.60
1.47	2.10	0.50

Similar ratios calculated from the results of the photolysis of solutions containing relatively higher concentrations of oxygen $[O_2] = 1.4 \times 10^{-3}$ M and $[C_2H_4] = 1.85 \times 10^{-3}$ M are higher than those calculated from the solutions containing lesser amount of oxygen. From the comparison of the above two tables it is obvious that there is a significant effect of $[C_2H_4]/[O_2]$ ratio on the photolysis products of ethylene-oxygen aqueous solutions. Due to the limited number of observations these results are of qualitative interest and a detailed study of the system is needed to understand the effect of ethylene-oxygen concentration.

Photolysis of Ethylene-Oxygen Aqueous Solutions without H_2O_2.

These experiments were carried out with unfiltered light with predominant emission at 2537 A°, but containing some mixture of light with the wavelengths in the region of 1850 A°. Under these conditions the organic products formed by the photolysis of ethylene-oxygen aqueous solutions $[C_2H_4] = 3.7 \times 10^{-3}$ M and $[O_2] = 1.0 \times 10^{-3}$ M were considered to be due to the free radicals H and OH, produced by photochemical decomposition of water. The results obtained are of purely qualitative interest because it was not known to what extent the products are formed by direct absorption of the light. Further, no facilities were available for the determination of the amount of energy deposited in the irradiated solutions.

Formaldehyde, formic acid, hydroxyethanal, acetaldehyde, an unidentified organic hydroperoxide (most likely to be hydroxy ethyl hydroperoxide) and hydrogen peroxide were the products detected in the irradiated solutions. From a limited number of observations it was shown that acetaldehyde and formaldehyde were the major products of the system, (Table 7). Hydroxyethanal and the organic hydroperoxide were formed in insignificant amounts. The formation of hydrogen peroxide was of interest and its actual yield must have been decreased by the photolytic decomposition by both 1850 and 2537 A°. It can be seen that the results are more or less similar to those obtained by γ-irradiating the ethylene-oxygen aqueous solutions.

Photolysis of Ethylene-Oxygen Aqueous Solutions Not Containing Hydrogen Peroxide.

Table 7 .

$[C_2H_4] = 3.7 \times 10^{-3}$ M $[O_2] = 1.0 \times 10^{-3}$ M

Product yield M x 10^5/L

H_2O_2	ROOH	CH_3CHO	HCHO	$HO.CH_2.CHO$	HCOOH
0.57	2.26	3.95	3.50	2.10	0.88
0.41	2.20	4.30	4.52	2.61	-
0.58	2.30	5.30	5.85	2.77	1.77
1.63	1.24	4.21	3.55	3.64	1.77
0.57	2.38	6.46	6.24	2.68	2.20

ROOH - Organic hydroperoxide.

3.6. REFERENCES

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CHAPTER 4

DISCUSSION

The action of ionizing radiations on water and aqueous solutions can be represented as follows:

$$H_2O \dashrightarrow e\ aq^- + H^+ + H + OH + H_2 + H_2O_2 \quad (1)$$

The hydroxyl radicals produced in the irradiated water are known to dehydrogenate dissolved hydrocarbons:

$$R\text{-}H + OH \dashrightarrow R\cdot + H_2O \quad (2)$$

In the presence of oxygen, the alkyl radicals produced in reaction (2) react quantitatively with oxygen to produce alkyl peroxy radicals which by subsequent reactions produce stable chemical products.

4.1. Oxidation of Ethane in Aqueous Solutions.

The competition experiments demonstrated that ethane is reactive towards hydroxyl radicals and under the conditions of both the radiolysis and photolysis, all the OH radicals would be efficiently scavenged by ethane:

$$CH_3.CH_3 + OH \dashrightarrow CH_3.CH_2\cdot + H_2O \quad (3)$$

$k_3 = 2.0 \times 10^9\ M^{-1}\ sec^{-1}$ at 20° C was estimated in the present work. In the presence of an adequate amount of dissolved oxygen, reaction (3) will be followed by addition of oxygen to ethyl radicals:

$$CH_3.CH_2\cdot + O_2 \dashrightarrow CH_3.CH_2.OO \quad (4)$$

The overall chemistry of the system is governed by the subsequent reactions of ethyl peroxy radicals.

In the hydrogen peroxide photolysis experiments, it was observed that the yields of acetaldehyde and ethanol together were greater than the apparent amount of hydrogen peroxide decomposed; indicating that hydrogen peroxide was reformed during the reactions of ethyl peroxy radicals. The stoichiometry of (5) appears to provide for the formation of acetaldehyde and hydrogen peroxide:

$$2\ CH_3.CH_2.OO \dashrightarrow 2\ CH_3.CHO + H_2O_2 \quad (5)$$

The small net decomposition of hydrogen peroxide results from the reactions of ethyl peroxy radicals not leading to the formation of hydrogen peroxide, the overall stoichiometry of which is represented by (6) :

$$2\ CH_3.CH_2.OO \longrightarrow CH_3\cdot CHO + CH_3.CH_2OH + O_2 \qquad (6)$$

If reactions (5) and (6) are the only reactions of ethyl peroxy radicals in this system, then it is apparent that the net amount of hydrogen peroxide decomposed should be equal to the ethanol yield. Table 2 shows that considering the inexact nature of the ethanol analysis the agreement between the two quantities is reasonable.

The irradiation at pH 1.2 and photolysis are alike in that acetaldehyde and ethanol are the only organic products formed and the ratios $[CH_3.CHO]/[CH_3.CH_2OH]$ are similar in both the cases; being 6.0 in the irradiated solutions and 9.0 in the photolysed solutions. In irradiated solutions, of course, the reactions of HO_2 radicals have also to be considered. At pH 1.2, the hydrated electrons will react with protons giving hydrogen atoms and these together with any other formed via routes not involving hydrated electrons will rapidly react with oxygen giving perhydroxyl radicals.

$$H + O_2 \longrightarrow HO_2 \qquad (7)$$

The results of pH 1.2 radiolysis suggest that the only reaction of these species is to give hydrogen peroxide by pairwise recombination:

$$2\ HO_2 \longrightarrow H_2O_2 + O_2 \qquad (8)$$

Hydrogen peroxide is thus a product of reactions (5) and (8) and for irradiated solutions at pH 1.2,

$$G\ (H_2O_2) = \tfrac{1}{2}\ G\ (CH_3.CHO - CH_3.CH_2OH) + \tfrac{1}{2}\ G_H + G_{H_2O_2}$$

Substituting the appropriate yields in the above expression, $G\ (H_2O_2)$ = 3.6 which is in agreement with the experimentally observed value of 3.7, (Table 1).

This reaction scheme appears to describe the main features of radiolysis at pH 1.2 and photolysis. However, it is important to point out that reaction scheme represents overall stoichiometric behaviour of the system and that reactions (5) and (6) are not necessarily mechanistic reactions.

At pH 5.5, 10.0 and 11.0, ethyl hydroperoxide appeared as a product at the expense of acetaldehyde (and probably ethanol). Johnson found that in neutral solutions, methyl hydroperoxide is formed in the radiolysis of methane-oxygen aqueous solutions but it is not a product in pH 1.2 radiolysis (Johnson 1955). This was ascribed to the fact that in neutral and alkaline solutions HO_2 radicals dissociate (pK = 4.5)

$$HO_2 \rightleftharpoons H^+ + O_2^- \qquad (9)$$

$$O_2 + e\,aq^- \longrightarrow O_2^- \qquad (10)$$

and it was suggested that O_2^- ions could react with methyl peroxy radicals giving ultimately methyl hydroperoxide:

$$CH_3.OO + O_2^- \longrightarrow CH_3.OO^- + O_2 \qquad (11)$$

$$CH_3.OO^- \xrightarrow{H^+} CH_3OOH \qquad (12)$$

It is proposed that a similar reaction accounts for the formation of ethyl hydroperoxide in the present work:

$$CH_3.CH_2.OO + O_2^- \xrightarrow{H^+} CH_3.CH_2OOH + O_2 \qquad (13)$$

Assuming that the stoichiometry of acetaldehyde formation is the same in neutral solutions as in acidic solutions; 5/6 of acetaldehyde yield is accompanied by the formation of hydrogen peroxide, then

$$G\ (H_2O_2) = 5\ /\ 12\ G\ (CH_3.CHO) + \tfrac{1}{2}\left[(G_{e\ aq^-} + G_H) - G\ (CH_3.CH_2OOH)\right] + G_{H_2O_2}$$

Substituting the appropriate yields $G\ (H_2O_2) = 2.3$, which is not in bad agreement with the experimentally observed value of 2.0, considering the variation in the initial G values of some of the products at pH 5.5.

The results of radiolysis at pH 10.0 and 11.0, show an increase in the yield of ethyl hydroperoxide compared with that at pH 5.5. This increase appears to be at the expense of acetaldehyde. G (H_2O_2), a proportion of which is due to (5), is likewise lower at at pH 10.0 and 11.0, than at pH 1.2 or 5.5. HO_2 radicals are largely dissociated at pH 5.5 and it is apparent that they are completely dissociated at pH 10.0 and 11.0. This therefore cannot be the cause of increased ethyl hydroperoxide yields at higher pH.

At about pH 11.0, the hydroxyl radicals dissociate according to (14):

$$OH \longrightarrow O^- + H^+ \qquad (14)$$

The nature and reactions of O^- ion are not very well known. However, the results of the present investigations show that total yield of organic products at both pH 10.0 and 11.0 approximates to G_{OH} It would thus appear that O^- dehydrogenates ethane as efficiently as unionised OH radicals.

A further support for the O_2 - mechanism for the formation of ethyl hydroperoxide in aqueous solutions is provided by the results of electron scavenging experiments at pH 5.5.

Nitrous oxide has been extensively used as an electron scavenger in both the gas phase and aqueous solution radiolysis and its reaction with electrons in the latter system has been represented as follows:

$$N_2O + e\,aq^- \longrightarrow N_2 + OH + OH^- \qquad (15)$$

Hydrogen atoms are not scavenged by nitrous oxide and in the presence of oxygen reaction (7) predominates. From the stoichiometry of (15) $G\ (N_2) = G_{e\ aq^-}$. The value of G (N_2) depends upon N_2O concentration as the following table from a recent publication shows;

10^4 M $[N_2O]$	G (N_2)
150	3.0
20.0	2.5
17.5	2.1
8.0	1.6

(Dainton and Walker 1965)

Hayon has attributed this increase in G (N_2) and consequently of $G_{e\ aq^-}$ to the scavenging of radicals by high scavenger concentration (Hayon 1965). in the regions of high radical concentrations or spurs. The decrease in G (N_2) at lower N_2O concentrations has been attributed to the competition of reactions of hydrated electrons other than (15).

In these experiments $[N_2O] = 1.0 \times 10^{-2}$M, was used and from the considerations of the results of Dainton, $G_{e\ aq^-} = 2.8$ has been assumed. Thus the total $G_{(reduction)} = 2.8 + 0.6$ (H atoms) $= 3.4$.

Addition of nitrous oxide in the radiolysis of ethane-oxygen aqueous solutions markedly decreased G $(CH_3.CH_2OOH)$ from 0.9 to 0.2. . It is suggested that the decrease is due to the competition of (15) and (10) with the subsequent lowering of O_2^- concentration. This mechanism would indicate that in solutions in which all the electrons were completely scavenged, G (organic product) should be equal to $G_{OH} + G_{e\ aq^-} = 2.2 + 2.8 = 5.0$. However the observed value was 3.3 which includes the unscavenged G (CH_3CH_2OOH) = 0.2. This residual yield of ethyl hydroperoxide is believed to arise from hydrogen atoms which are not scavenged by nitrous oxide. Although ethanol determinations were not made in these experiments a reasonable estimate can be made from the acetaldehyde to ethanol ratio observed in the radiolysis at pH 1.2 and photolysis experiments. This would not be expected to be in excess of G $(CH_3.CH_2OH) = 0.5$ Adding this quantity, G (total organic products) = 3.8 which is 1.2 units lower than the expected value. G $(H_2O_2) = 3.3$ was also observed in these experiments but only a part of it can be accounted for from the known sources:

$$G\ (H_2O_2) = 5/12\ G\ (CH_3.CHO) + G_{H_2O_2} + \tfrac{1}{2}\left[G_H - G\ (CH_3.CH_2OOH)\right]$$

Substituting the appropriate yields G $(H_2O_2) = 2.2$ which is substantially lower than the experimentally observed value. It is probable that the remaining yield is associated with $G_{e\ aq^-}$ that does not appear as organic products, presumably by some reactions of N_2O^- intermediate. A more complete analysis of the products, in particular of nitrogen is essential to understand the detailed mechanism of electron scavenging in this system.

Hydrogen peroxide, another efficient electron scavenger, was used under the same conditions as nitrous oxide. This also suppressed the formation of ethyl hydroperoxide presumably through the competition of (16):

$$H_2O_2 + e\,aq^- \dashrightarrow OH + OH^- \qquad (16)$$

The concentration of hydrogen peroxide used was sufficient to scavenge 75 % of the electrons and the corresponding reduction in G ($CH_3.CH_2OOH$) from 0.9 to 0.6, was consistent with this value. The residual yield of organic peroxide was presumably due to the unscavenged electrons and the hydrogen atoms which are thought to be formed in neutral solutions ($G_H = 0.6$). The predicted increase in G (organic products) from 2.5 in ordinary neutral solution to 4.1 in hydrogen peroxide -containing solutions, was also observed. This value includes an estimated G (ethanol) = 0.5. Due to the inexact nature of ethyl hydroperoxide analysis and uncertainty about the ethanol yield, it is difficult to make a quantitative assessment of electron scavenging in this system . However, it is reasonable to say that these experiments offer further evidence of the O_2^- mechanism of ethyl hydroperoxide formation.

Nitrate ions were also used as electron scavenger in a limited number of experiments. Appleby and others had suggested that electron scavenging by nitrate ions, as in the case of nitrous oxide and hydrogen peroxide, is accompanied by hydroxyl radical production (Appleby 1963):

$$NO_3^- + e\,aq^- \dashrightarrow NO_2^- + OH + OH^- \qquad (17)$$

These results showed that whereas the addition of nitrous oxide and hydrogen peroxide both increased G (organic product) and also resulted in decreased G (organic peroxide), no comparable increase in G (organic product) or decrease in G (organic peroxide) was observed in the case of nitrate ions when used in solution at concentrations as high as 10^{-1}M; G ($CH_3.CHO$) = 1.6 (1.6), G ($CH_3.CH_2OOH$) = 1.08 (0.9) and G (H_2O_2) = 1.5 (2.0). The figures in brackets refer to yields at pH 5.5 irradiations not containing the scavenger.

Recent work on the radiation chemistry of nitrate ions has shown that in neutral deaerated solutions both electrons and hydrogen atoms reduce nitrate to nitrite:

$$NO_3^- + e\ aq^- \dashrightarrow NO_3^{-2} \qquad (18)$$

$$NO_3^{-2} + H^+ \dashrightarrow NO_2 + OH^- \qquad (19)$$

$$NO_3^- + H \dashrightarrow NO_2 + OH^- \qquad (20)$$

$$2\ NO_2 + H_2O \dashrightarrow NO_2^- + NO_3^- + 2\ H^+ \qquad (21)$$

The intermediate radical ion NO_3^{-2} was tentatively identified by electron paramagnetic resonance spectrum of irradiated potassium nitrate crystal (Cunningham 1962). According to above mechanism G (NO_2^-) in deaerated solutions = $\frac{1}{2}$ ($G_{e\ aq^-} + G_H$). Appleby and others in the study of radiolysis of deaerated propanol-nitrate aqueous solutions measured G (NO_2^-) = 2.52, at 10^{-3}M nitrate concentration. This value being twice the value predicted by above mechanism lead Appleby to suggest that OH radicals are produced in reaction (17). Allan confirmed these observations but suggested that observed nitrite yields could be explained by a reaction of organic radicals with the intermediate NO_3^{-2} (Allan 1964):

$$(CH_3)_2.COH + NO_3^{-2} \dashrightarrow CH_3.CO.CH_3 + NO_2^- + OH^- \qquad (22)$$

His own work on the radiolysis of methanol-nitrate aqueous solutions supports the reactions of type (22):

$$CH_3OH + OH \dashrightarrow .CH_2OH + H_2O \qquad (23)$$

$$.CH_2OH + NO_3^{-2} \dashrightarrow HCHO + NO_2^- + OH^- \qquad (24)$$

In the presence of nitrate ions an actual increase in G(CH_2O) was observed. In deaerated solutions not containing nitrate ions the predominant reaction of the organic radicals produced in (23) is to give glycol by dimerisation. In oxygenated solutions however, the organic radicals give organic peroxy radicals which by other reactions give organic products:

$$\cdot CH_2OH \ + \ O_2 \dashrightarrow O_2.CH_2OH \dashrightarrow \text{products} \qquad (25)$$

Allan attributed the reduction of G (NO_2^-) from $G_{e\ aq}^-$ to $\frac{1}{2}\,G_{e\ aq}^-$ in oxygenated solutions to the competition of (25) and (24).

The presence of oxygen in irradiated solutions drastically reduces G (NO_2^-). This cannpt be entirely due to the competition of reactions (10) and (18), as in solutions containing $NO_3^- = 10^{-1}M$ all the electrons are expected to react by (18); $k_{10}/k\ 18 = 1.15$ determined by Allan. It would thus appear that oxygen is oxidizing the precursors of nitrite back to nitrate (Hyder 1965).

The increase in G (NO_2^-) at higher nitrate concentration in solutions has been observed by several workers. Allan suggested that this effect could be due to the scavenging of electrons from the spurs. This suggestion is supported by a recent work of Hayon who showed that oxidizing solutes as nitrous oxide, oxygen, and nitrate ions, when present in concentrations greater than $10^{-2}M$ can scavenge electrons from the spurs (Hayon 1965).

In the present experiments the concentration of nitrate used was sufficient to scavenge 99 % of electron yield . In the light of preceding discussion, the most probable explanation of the relatively unchanged yield of ethyl hydroperoxide is that a proportion of NO_3^{-2} reacts with ethyl peroxy radicals giving ultimately ethyl hydroperoxide:

$$CH_3.CH_2.OO \ + \ NO_3^{-2} \dashrightarrow CH_3.CH_2.OO^- \ + \ NO_3^- \qquad (26)$$

Assuming that the stoichiometry of acetaldehyde formation is the same to that in the absence of nitrate ions; 5/6 of acetaldehyde yield is accompanied by the formation of hydrogen peroxide,

$G\ (H_2O_2) = 5/12\ G\ (CH_3.CHO) + \frac{1}{2}\,G_H \ + \ G_{H_2O_2}$. Substituting the appropriate yields $G\ (H_2O_2) = 1.6$, which is in agreement with the observed value of 1.5. The contribution to hydrogen peroxide from hydrogen atoms could be reduced by up to 20 % as a result of the competition of (7) and (20). Similarly hydrated electron yields can be accounted for in these experiments,

$$G_{e\ aq^-} = G\ (CH_3.CH_2OOH) + 2\ G\ (NO_2^-)$$

Substituting the appropriate values from Table 1, $G_{e\ aq^-} = 3.48$. The higher calculated values of $G_{e\ aq^-}$ in this system are presumably due to the scavenging of reducing radicals from the spurs.

It is interesting to compare the results of ethane oxidation in aqueous solutions with those of low temperature oxidation initiated by other methods. Watson and Darwent found that in the gas phase mercury photosensitised oxidation of ethane, ethyl hydroperoxide was the major product (Watson and Darwent 1957). Its formation was ascribed to the reaction:

$$CH_3.CH_2.OO\cdot + HO_2 \dashrightarrow CH_3.CH_2OOH + O_2 \qquad (27)$$

The occurrence of a similar reaction in the gas phase oxidation of iso-butane has been demonstrated in a latter work (Bell and McDowell 1961). It is however interesting that reaction (27) involving undissociated perhydroxyl radicals is not important in aqueous solutions.

In studies on the reactions of ethyl peroxy radicals generated by gas phase photochemical decomposition of ethyl iodide (Heicklen and Johnston 1962) and azoethane (Dingledy and Calvert 1963), in the presence of oxygen, acetaldehyde and ethanol were the major products. There is substantial evidence that ethoxy radicals are involved in the formation of these products:

$$2\ CH_3.CH_2.OO \dashrightarrow 2\ CH_3.CH_2.O + O_2 \qquad (28)$$

$$2\ CH_3.CH_2.O \dashrightarrow CH_3.CHO + CH_3.CH_2OH \qquad (29)$$

It can be seen that this sequence has the overall stoichiometry expressed by (6). In the experiments of Calvert the yields of ethanol and acetaldehyde were equal but Heicklen observed that yield of acetaldehyde was always greater than that of ethanol. This was accounted for, in part, by a reaction between ethoxy radicals and oxygen:

$$CH_3.CH_2.O + O_2 \dashrightarrow CH_3.CHO + HO_2^{\cdot} \qquad (30)$$

The predicted effect of oxygen concentration on the competition of (30) and (29) was noted by Heicklen. It is apparent that reaction sequence (28), (30) and (8) account for the stoichiometry of (5). It would thus seem probable that ethoxy radicals are also involved in the oxidation of ethane in aqueous solutions, and that the observed stoichiometry can be explained by reactions (28), (29) and (30) together with (8) or a stoichiometric equivalent. Two observations however, suggest that in aqueous solutions these reactions do not occur homogeneously, but rather in solvent cages. No effect of oxygen concentration on G ($CH_3.CHO$) or G (H_2O_2) was noted; the dose-yield plots of these products were linear up to the highest dose (4.5×10^{21} eV/L) at which the oxygen concentration would be depleted to half the value of initial oxygen concentration. In photolysis of ethane-oxygen aqueous solutions at pH 5.5, where any HO_2 formed would dissociate to O_2^-, no ethyl hydroperoxide was detected, suggesting that freely diffusing perhydroxyl radicals are not produced homogeneously. If this is the case then HO_2 radicals must react within the cage:

$$CH_3.CH_2.O + HO_2 \dashrightarrow CH_3.CHO + H_2O_2 \qquad (31)$$

It would be useful to test this by irradiating ethane solutions saturated with oxygen at pressures higher than those used in this work. Another possible way of testing the proposed reactions of ethoxy radicals would be to study the effect of dose rate on the 2
yield of products at pH 1.2. It can be seen that $k_{29} \propto [CH_3.CH_2.O]$ and $k_{31} \propto [CH_3.CH_2.O]$. A change in dose rate would affect the competition of (29) and (31).

The importance of reactions similar in stoichiometry to (5) is well recognised in the radiation chemistry of aqueous solutions of organic compounds (Garrison 1957). On the other hand there are a few examples of stoichiometry expressed by (6). Radiolysis of aqueous solutions of acetic acid shows that the reactions of peroxy radical $OO.CH_2.COOH$ are similar to those of ethyl peroxy radicals in that both the reaction types (5) and (6) are important, although in that case they appear to occur to an equal extent (Garrison 1959).

The rôle of alkoxy radicals in the oxidation of hydrocarbons.

From the preceding discussion it appears that alkoxy radicals perhaps do play an important part in the oxidation of hydrocarbons in gas phase and aqueous solutions. However, the possibility of formation and subsequent reactions of these species in the radiation-induced oxidation of hydrocarbons in aqueous solutions has not been mentioned. The evidence, obtained in gas phase only, is indirect; addition of alkoxy radical scavengers decrease the yield of products dependent upon R.O. It seems imperative to devise methods of identifying these radicals, preferrably by physical methods. The e. s. r. technique has been successfully used in the past to identify radicals and ions. Some differences in the electron spin resonance spectrum of R.OO and R.O would be expected, due to different environment of the unpaired electron in these species. The success of such a physical observation depends, besides other factors, on the lifetime of these radicals; it is not possible to observe species by e. s. r. having a lifetime less than 10^{-4} sec.

It is useful to consider possible methods of production of R.O other than (28). Radiolysis of neutral solutions of alkyl hydroperoxides; ethyl hydroperoxide or methyl hydroperoxide may lead to the formation of alkoxy radicals in aqueous solutions:

$$CH_3.CH_2.OOH \quad + \quad e\ aq^- \longrightarrow CH_3.CH_2.O \quad + \quad OH^- \qquad (32)$$

It would be necessary to carry out the radiolysis in presence of a suitable hydroxyl radical scavenger to prevent reaction (33)

$$CH_3.CH_2OOH \quad + \quad OH \longrightarrow \text{products} \qquad (33)$$

In view of the expected high reactivity of R.O radicals it would be easier to observe the formation of these species in frozen aqueous solutions by e. s. r. method.

Perhaps a simpler and cleaner method of producing these species is by the photolysis of aqueous solutions of methyl or ethyl hydroperoxide by light of wavelength 2537 A°.

$$CH_3.CH_2OOH \xrightarrow{hv} CH_3.CH_2.O + OH \qquad (34)$$

It can be seen that the process is identical to the photochemical decomposition of hydrogen peroxide to hydroxyl radicals and likewise could be used in both gas phase and aqueous solutions. Both these methods would produce alkoxy radicals in isolation rather than pairwise as in (28). It should be possible to observe the reaction of these species under the conditions where (29) and (30) can compete homogeneously and the effect of oxygen concentration and dose rate on these reactions could be compared with the similar effects in the irradiated ethane-oxygen aqueous solutions

4.2. Oxidation of Methane in Aqueous Solutions

In the present work, methane-oxygen aqueous solutions were irradiated and photolysed under different conditions of pH and solute concentration. Formaldehyde, methanol, formic acid, methyl hydroperoxide and hydrogen peroxide were the products detected in this system. Various mechanisms leading to the formation of these products will be discussed in the light of information available from the gas phase reactions of methyl peroxy radicals and from the reactions of alkyl peroxy radicals in general.

The reaction of hydroxyl radicals with methane in aqueous solutions produces methyl radicals:

$$CH_4 + OH \longrightarrow CH_3\cdot + H_2O \qquad (35)$$

k_{35} was estimated to be about $1.3 \times 10^7 M^{-1} sec^{-1}$ at 20°C. It is interesting to compare this value with that of the rate constant of reaction (3). $k_3/k_{35} = 100$ determined in the present work is in clear disagreement with the value of about 2.38 determined previously (Berces 1961). It is difficult to attribute this large difference in the ratios obtained in the two works to any particular cause. However, consideration of another ratio of rate constants k_{36}/k_{35} in gas phase and aqueous solutions appear to support the value of k_{35} obtained in this work.

$$CO + OH \dashrightarrow CO_2 + H \qquad (36)$$

In the gas phase $k_{36}/k_{35} = 100$ can be extrapolated from the work of Hoare who measured the relative rates of methane and carbon monoxide reactivity with hydroxyl radicals (Hoare 1966). Using data for the rate of reaction of OH with CO in aqueous solutions and our value of k_{35}, $k_{36}/k_{35} = 44$, (Buxton and Wilmarth 1963). The agreement with these two values is reasonable and supports the belief that k_{35} is much slower than k_3. Hoare has also found that in gas phase $k_{37}/k_{35} = 40$ at 458C; again indicating that reaction (35) is a comparatively slow reaction.

$$HCHO + OH \dashrightarrow \text{products} \qquad (37)$$

The products of methane oxidation in aqueous solutions, viz formaldehyde are highly reactive towards hydroxyl radicals ($k_{37}/k_{35} = 100$) and as a result, the formaldehyde dose-yield curves in irradiated solutions saturated with methane at atmospheric pressures soon come to a plateau concentration. This situation was remedied by increasing methane-oxygen concentration in solution by putting higher pressures using a pressure vessel.

In acidic solutions, saturated with gases at atmospheric pressures a large product deficiency was observed. Increase in the concentration of methane-oxygen mixture or an increase in pH from 1.2 to 2.0, increased the product yield. At pH 2.0, formic acid and methanol were also detected. The different initial G values of formaldehyde at various methane-oxygen concentrations in sulphuric acid solutions suggested that a reaction, not involving hydroxyl radicals per se, is in competition with (35). From two recent studies it is known that reaction (38) is a major reaction in irradiated sulphuric acid solutions, (Boyle 1959) and (Hochanadel 1962).

$OH + HSO_4^- \dashrightarrow HSO_4 + OH^-$ (38)

$k_{38} = 2.2 \times 10^7\ M^{-1}\ sec^{-1}$ was determined in the latter work. Boyle and coworkers studied the role of sulphuric acid (0.1N) in the radiolysis of cerous-ceric aqueous solutions and found that in addition to reaction (38), following are the more important processes:

$HSO_4 + HSO_4 \dashrightarrow H_2S_2O_8$ (39) (Boyle 1962)

$OH + HSO_4 \dashrightarrow H_2SO_5$ (40)

$HSO_4 + H \dashrightarrow H_2SO_4$ (41)

All the species produced as a result of these reactions were identified by the authors. The reaction of hydroxyl radicals with undissociated sulphuric acid was considered to be unimportant. Sworski supported this assumption by measuring $k_{42} = 4.4 \times 10^5\ M^{-1}sec^{-1}$.

$OH + H_2SO_4 \dashrightarrow HSO_4 + H_2O$ (42) (Sworski 1962)

In the present system, under acid conditions, reaction (38) is important because k_{35} and k_{38} are of the same order. The calculated concentrations of hydrosulphate ions in pH 1.2 and 2.0 solutions are $6.3 \times 10^{-2}M$ and $7.95 \times 10^{-3}M$ respectively. From the considerations of rate constants of (35) and (38) and methane and hydrosulphate concentrations in solutions saturated with gases at atmospheric pressures, all hydroxyl radicals would be expected to react by (38). However, examination of the tables 3 and 4 shows that under the conditions mentioned some formaldehyde is formed. It would appear that HSO_4 radicals are also capable of attacking methane in a manner similar to hydroxyl radicals:

$HSO_4 + CH_4 \dashrightarrow CH_3 + H_2SO_4$ (43)

However, the low initial yields of formaldehyde at low methane concentration suggest that not all the HSO_4 radicals react by (43). In the ethane-oxygen radiolysis and photolysis carried out in the presence of sulphuric acid solutions (0.1N) about 50 % of hydroxyl radicals would be expected to react by (38) and it was found that the yield of organic products = G_{OH}; indicating that all the HSO_4 radicals dehydrogenate ethane producing ethyl radicals.

In order to minimise the effect due to sulphuric acid, the pH was kept at 2.0 and methane-oxygen concentration was increased by a factor of about 20. Under these conditions 60 % of the OH radicals reacted by (35). For the purpose of the present discussion reference will only be made to those experiments which were carried out at high methane-oxygen pressures.

<u>Reactions of methyl peroxy radicals in gas phase.</u>

Collective information from gas phase oxidation of methyl radicals suggest that formation of methyl peroxy radicals is the first step in such systems:

$$CH_3 + O_2 \longrightarrow CH_3.OO \qquad (44)$$

The formation of this radical has been tentatively demonstrated, (McKeller and Norrish 1961). The products of subsequent reactions of methyl peroxy radicals in both the gas phase and aqueous solutions are similar; radiolysis of methane-oxygen gas mixtures produced methyl hydroperoxide as the main product (Johnson and Salmon 1961). More recently it has been shown that formaldehyde, methanol and formic acid are less important product in the gas phase radiolysis, (Hearne and Hummel 1964) and (Clay and Rosen). However, it is unlikely that the reactions in these systems are entirely radical in nature.

In the past few years, attempts have been made to study the oxidation of methyl radicals and subsequent reactions of methyl peroxy radicals under ~~the~~ conditions in which least complications due to other species (e.g. the presence of ionic species in the radiolysis of gaseous mixtures), are likely to occur. Information obtained by using improved analytical techniques (long path spectrometry) has given some insight into the possible intermediate steps leading to the formation of the observed products. The complete picture as to what happens after reaction (44) is still not clear but nevertheless, these studies have helped to do away with some of the more improbable mechanims. Some of the proposed mechanisms are still speculative while for others kinetic and thermodynamic data is available.

Calvert and Dever investigated the photochemical decomposition of methyl iodide in oxygen rich media at 25° C and found that apart from the main products; formaldehyde and methanol formed in 1:1 ratio, methyl hydroperoxide was also formed in detectable quantities, Calvert and (Dever 1962). The excellent studies of Subbaratnam and Calvert have confirmed the observations of Calvert and Dever and have shown that methoxy radicals are involved in the formation of these products (Subbaratnam and Calvert 1962):

$$2\ CH_3.OO \longrightarrow 2\ CH_3.O + O_2 \qquad (45)$$

$$CH_3.O + CH_3.OO \longrightarrow CH_3OOH + HCHO \qquad (46)$$

Formation of methyl hydroperoxide by dehydrogenation of hydrocarbon or another methyl peroxy radical by methyl peroxy radical was ruled out on the basis of thermodynamic considerations. Methanol and formaldehyde were considered to be formed via (47):

$$2\ CH_3.O \longrightarrow CH_3OH + HCHO \qquad (47)$$

The evidence for the formation of methoxy radicals was based on the observation that addition of small quantities of formaldehyde in the photolysis cell decreased the formation of methyl hydroperoxide:

$$CH_3.O + HCHO \longrightarrow CH_3OH + .CHO \qquad (48)$$

An equivalent increase in the yield of methanol as predicted by (48) was observed at the same time.

Reaction (49) appeared to be unimportant as dimethyl peroxide was not detected among the initial products of the photolysis.

$$CH_3.O \;+\; CH_3.O \dashrightarrow CH_3OOCH_3 \qquad (49)$$

Heicklen and Johnston studied the oxidation of methyl radicals under similar conditions and their results also supported the formation and subsequent reactions of methoxy radicals (Heicklen and Johnston 1962). In this study the initial rate of formation of formaldehyde was greater than that of methanol. Reaction (50) was proposed to account for extra yield of formaldehyde:

$$CH_3.O \;+\; O_2 \dashrightarrow HCHO \;+\; HO_2 \qquad (50)$$

The predicted effects of oxygen concentration on the competition of (50) and (47) were observed by the authors.

Two recent studies by Linnet and coworkers, have indicated that the reactions of methoxy radicals do not govern the overall chemistry of these systems (Barker 1963, Farren 1964). Their results show that reactions (51) and (52) are more important than (44) and (45):

$$CH_3 \;+\; O_2 \dashrightarrow HCHO \;+\; OH \qquad (51)$$

$$CH_3.OO \;+\; OH \dashrightarrow CH_3OH \;+\; O_2 \qquad (52)$$

It is apparent that methanol and formaldehyde are formed by two different routes. Reaction (51) is a well known reaction in the oxidation of methyl radicals at high temperatures (Hoare 1966) but it is not a predominant reaction at room temperatures. In aqueous solutions, (51) would appear to be unlikely because of the rapid stabilisation of methyl peroxy radicals in the liquid. Further more, in aqueous solutions, the occurrence of this reaction will induce a chain oxidation of methane. Since no such observation was made it is evident that this reaction does not occur in aqueous solutions. The evidence for reaction scheme described by Calvert and Heicklen and Johnston is convincing and will be the basis for the present discussion. The possible methods of production and identification of alkoxy radicals in general have been discussed in the reactions of ethyl peroxy radicals.

Reactions of methyl peroxy radicals in aqueous solutions.

The formation of ethyl peroxy radicals was assumed to explain the results obtained in the radiolysis and photolysis of ethane-oxygen aqueous solutions. Although no direct physical evidence is available, the formation of methyl peroxy radicals has been assumed to interpret the results obtained by the radiolysis and photolysis of methane-oxygen aqueous solutions.

In the present work photolysis of methane-oxygen aqueous solutions at pH 5.5, gave methanol, and formaldehyde only. The formation of these products could be expressed by the stoichiometry of (53):

$$2\ CH_3.OO \dashrightarrow CH_3OH + HCHO + O_2 \qquad (53)$$

It can be seen that reactions (45) and (47) known to occur in gas phase, have the same overall stoichiometry as (53).

In the radiolysis at pH 1.2 and 2.0, observed G (H_2O_2) was in excess of the amount expected from $G_{H_2O_2}$ and reaction (8).

$$G\ (H_2O_2) = G_{H_2O_2} + \tfrac{1}{2} G_H$$
$$= 2.6$$

Experimentally observed G (H_2O_2) = 3.5 (Table 3). Consequently hydrogen peroxide must also be formed during reactions producing organic products. An obvious possibility is reaction (54), possibly proceeding through methoxy intermediates as in (50):

$$2\ CH_3.OO \dashrightarrow 2\ HCHO + H_2O_2 \qquad (54)$$

However, at this pH, methanol was also found to be a product and it is not unreasonable to suppose that this may have originated via (53). Thus the extra hydrogen peroxide originating in this fashion would be given by $\frac{1}{2}$ (G HCHO - G CH_3OH). The measured methanol yields were not precise enough for this calculation to be performed accurately but an estimate of G (CH_3OH) can be made from G_{OH} - G

(HCHO + HCOOH) = G (CH_3OH) = 0.6. A value of G (H_2O_2) = 2.9 evaluated from this calculation is still smaller than the observed (G = 3.5). However, if formic acid is also accompanied by the formation of hydrogen peroxide according to:

$$CH_3.OO + O_2 \longrightarrow HCOOH + HO_2 \qquad (55)$$

then G (H_2O_2) = 2.9 + $\frac{1}{2}$ G (HCOOH) = 3.38, in good agreement with the measured value. Alternatively, it is possible that both methanol and formic acid arise from reaction:

$$CH_3OO + CH_3.O \longrightarrow CH_3OH + HCOOH \qquad (56)$$

Since within the wide limits of error G (CH_3OH) = G (HCOOH), on this basis, hydrogen peroxide would accompany the formation of all the formaldehyde predicting G (H_2O_2) = 2.6 + $\frac{1}{2}$ G (HCHO) = 3.2, somewhat lower than that observed.

No firm choice can be made between these mechanisms; in particular neither would appear to predict a pH dependent yield of formic acid such as has been observed; Formic acid was a product in acidic solutions but it was not detected in neutral solution photolysis. It is interesting to note that formic acid was also a product in the gas phase oxidation of methyl radicals and its formation was explained via (56) (Dever and Calvert 1962).

During the discussion of the reactions of methyl peroxy radicals in aqueous solutions it was pointed out that methoxy radicals might be involved in the formation of observed products; stoichiometry of (53) and (54) is the same as that of (45), (47), (50) and (8). One of the formic acid mechanisms also involves the participation of methoxy radicals. Our results however suggest that homogeneous formation of these species in aqueous solutions is unlikely. The effect of oxygen concentration at a constant methane concentration was examined on the possible competition of (50) and (47). It was found that a 10 fold increase in oxygen concentration did not alter G (HCHO) or G (H_2O_2)at pH 2.0. However, if the reactions occur in solvent cages, no effect of oxygen concentration could be expected in the concentration range used.

Irradiations at pH 5.5, showed that methyl hydroperoxide was the major organic product, G = 1.65. Like ethyl hydroperoxide it is not formed in acidic solution radiolysis or photolysis at pH 5.5, and 2.0. Some aspects of the mechanism involved in the formation of this product were discussed in connection with the formation of ethyl hydroperoxide:

$$CH_3.OO + O_2^- \longrightarrow CH_3.OO^- + O_2 \qquad (11)$$

$$CH_3.OO^- + H^+ \longrightarrow CH_3OOH \qquad (12)$$

When nitrous oxide (5×10^{-2} M), was added to the methane-oxygen solutions G (CH_3OOH) decreased from 1.65 to 1.15, giving some support to the belief that O_2^- ions were involved in the hydroperoxide formation via (11). The addition of this concentration of nitrous oxide would not have entirely eliminated O_2^- ions since at the concentration used 10 % of the hydrated electrons ($G_{e\ aq^-} = 3.4$) would still have reacted with the oxygen present. Furthermore, O_2^- ions would also have been formed by the reaction of hydrogen atoms with oxygen.

In the unscavenged radiolysis approximately half the O_2^- yield appeared to react with methyl peroxy radicals to give methyl hydroperoxide. In the presence of nitrous oxide however, the $G(O_2^-)$ would be lowered and G ($CH_3.OO$) increased and it is not unreasonable to suppose that more than half of the O_2^- ions would react via (11). Thus in the nitrous oxide scavenged system something between G (CH_3OOH) = 0.4 to 0.9 can reasonably be attributed to reactions of the O_2^- ions not eliminated by nitrous oxide.

The observed G (CH_3OOH) under these conditions was found to be 1.15 and there would appear to be a source of methyl hydroperoxide not involving O_2^-.

It is known that electron scavenging by N_2O is accompanied by hydroxyl radicals production such that G (organic products) = $G_{OH} + G_{e\ aq^-} = 5.0$. However, in this system, the observed

G(organic products) was 2.85, significantly less than the expected value. Although methanol determinations were not made, some contribution to G (organic products) would be expected from this product. However, it is unlikely that all the missing yield, G = 2.0. is due to methanol. In these experiments, G (H_2O_2) = 2.4, was also measured: apart from the molecular yield. It is obvious that there must be other sources of the hydrogen peroxide yield and apart from the contribution due to the molecular yield, the possibility of reaction (54) producing formaldehyde and hydrogen peroxide has been discussed before. If it is assumed that all the formaldehyde yield originates via (54) then,

$$G\ (H_2O_2) = 0.7 + \tfrac{1}{2}\, G\ (HCHO) = 1.55,$$

which is still substantially smaller than the observed value.

Although the lack of complete product analysis in this system makes further detailed consideration impossible, it is interesting to note that the deficiency in measured organic product yield, G = 2.0 appears to be related to the unexplained excess of hydrogen peroxide G = 1. This suggests that those electrons, which, while reacting with nitrous oxide, do not give rise to methyl hydroperoxide or formaldehyde are ultimately involved in reactions producing hydrogen peroxide.

From the preceding discussion, it is apparent that the nature of reactions occurring in electron scavenging systems is not very well understood. This is partly due to the fact that important parameters such as G (CH_3OH) and G (N_2) are not known. However, these experiments have shown that O_2^- ions are involved in the formation of at least a proportion of the methyl hydroperoxide.

In the neutral solutions, not containing nitrous oxide,

$$G\ (H_2O_2) = G_{H_2O_2} + \tfrac{1}{2}\, G\ (HCHO) + \tfrac{1}{2}\left[(G_{e\ aq^-} + G_H) - G\ (CH_3OOH)\right]$$

putting the values of various quantities, G (H_2O_2) = 1.81, which is somewhat lower than the experimentally measured value of 2.1. It can be seen that for this calculation all the formaldehyde yield was assumed to be accompanied by hydrogen peroxide formation.

Irradiation of methane (2.5×10^{-2} M), hydrogen (5.3×10^{-3} M) and oxygen (2.0×10^{-3} M) solutions were carried out in order to confirm the approximate value for $k_{OH + CH_4}$ obtained elswhere. The expected reduction in the organic products was obtained and a rate constant ratio $k_{OH + CH_4} / k_{OH + H_2} \sim 2$ calculated. G (H_2O_2) was found to increase from 2.1, in the absence of hydrogen to 2.4 in the presence of that scavenger. On the basis of the mechanisms discussed above a value of G (H_2O_2) can be predicted,

$$G\ (H_2O_2) = G_{H_2O_2} + \tfrac{1}{2}\ G\ (HCHO) + \tfrac{1}{2}\left[G(\text{reduction}) - G\ (CH_3OOH)\right] + \tfrac{1}{2}\ G_{OH} - G\ (\text{total organic products})$$

= 2.3, agreeing with the measured value of 2.4.

4.3. Oxidation of Ethylene in Aqueous Solutions.

Photolysis of hydrogen peroxide solutions containing ethylene-oxygen mixtures resulted in the formation of formaldehyde, formic acid, hydroxyethanal and hydroxy ethyl hydroperoxide. The yields of these products per molecule of hydrogen peroxide decomposed are given below:

pH	HCHO	$HO.CH_2.CHO$	HCOOH	$HO.CH_2.CH_2OOH$	
5.5	0.95	0.87	0.6	0.27	
	0.91	0.94	0.44	0.32	
	0.93	0.94	0.28	0.31	
	1.4	0.84	0.49	0.27	
	1.0	0.91	0.47	0.30	
	1.1	0.98	0.47	0.21	
	0.94	1.04	0.48	0.27	
	1.1	0.99	0.47	0.30	
	1.03	0.95	0.50	0.28	Average values
2.0	1.1	1.1	0.11	0.21	
	1.1	1.15	0.26	0.11	
	1.0	1.1	0.14	0.16	
	1.08	1.1	0.17	0.16	Average values

From the observed hydrogen peroxide decomposed (Table 5), it is apparent that hydrogen peroxide is also a product of the photolysis. On the basis that the formation of each C-C product requires 1 OH and each single carbon product requires $\frac{1}{2}$ OH, it can be shown that each molecule of hydrogen peroxide decomposed resulted in the formation of 0.3 and 0.41 molecules of hydrogen peroxide at pH 5.5 and 2.0 respectively. It is probable that some of the regenerated hydrogen peroxide is associated with the formation of hydroxyethanal:

$$2\ HO.CH_2.CH_2.OO \longrightarrow 2\ HO.CH_2.CHO + H_2O_2 \qquad (57)$$

Similar reactions (or stoichiometric equivalents) also appear to account for the hydrogen peroxide being a product in the photolysis and radiolysis of ethane-oxygen aqueous solutions. The fact that hydrogen peroxide was a product in this system was also demonstrated by the comparison of the rate of decomposition of hydrogen peroxide in deaerated and oxygenated solutions containing a suitable hydroxyl radical scavenger. It was found that for a given initial concentration the rate of decomposition of hydrogen peroxide in deaerated solutions was consistently greater than that in oxygenated solutions(Appendix 9 & 10). This is due to the regeneration of hydrogen peroxide, the ratio being 1 : 1.28 at pH 5.5 and 1 : 1.6, at pH 2.0.

The formation of formaldehyde and formic acid requires the breaking of C-C bond. The following sequence of reaction seems reasonable to account for the formation of these products:

$$2\ HO.CH_2.CH_2.OO \longrightarrow 2\ HO.CH_2.CH_2.O + O_2 \qquad (58)$$

$$HO.CH_2.CH_2.O + O_2 \longrightarrow HO.CH_2.OO + HCHO \qquad (59)$$

$$2\ HO.CH_2.OO \longrightarrow 2\ HCHO + H_2O_2 + O_2 \qquad (60)$$

$$2\ HO.CH_2.OO \longrightarrow HCOOH + HCHO + H_2O + O_2 \qquad (61)$$

Reactions (60) and (61) were proposed to explain some features of the radiolysis of methanol aqueous solutions (Allan 1964). This scheme also accounts for the formaldehyde yields being larger than those of formic acid. However, Allan found that the yield of formic acid from the $HO.CH_2.OO$ radicals was very small ($G = 0.2$ in a total of $G = 2.0$). On the other hand these experiments would suggest that in neutral solutions a considerable proportion of hydroxy methyl peroxy radicals give formic acid. It is probable that in neutral solutions formic acid is also formed via (62):

$$HO.CH_2.OO + HO.CH_2.CH_2.OO \dashrightarrow HO.CH_2.CHO + HCOOH + H_2O_2 \qquad (62)$$

Reactions involving two different radicals would be expected to be of similar probability as bimolecular reactions involving same radicals.

Hydroxy ethyl hydroperoxide is formed in minor quantities in both the neutral and acidic solutions and on this basis this product is unlikely to be formed via the O_2^- mechanism proposed for the formation of methyl and ethyl hydroperoxides. Reaction (63) also seems unlikely as substantial changes in hydrogen peroxide concentration did not affect the yield of this product.

$$HO.CH_2.CH_2.OO + H_2O_2 \dashrightarrow HO.CH_2.CH_2OOH + HO_2 \qquad (63).$$

It is probable that this product originates via (64)

$$HO.CH_2.CH_2.O + HO.CH_2.CH_2.OO \text{ --- } HO.CH_2.CH_2OOH + HO.CH_2.CHO \qquad (64)$$

The reactions of this type ($R.OO + R.O \dashrightarrow R.OOH + R.CHO$) are well known in the gas phase oxidation of hydrocarbons at room temperature and there too, organic hydroperoxides are formed in minor quantities compared with the yields of aldehydic and alcohol products. It is interesting to observe that an organic hydroperoxide was also formed in the photolysis of propylene-oxygen aqueous solutions under identical conditions (Clay and Khan private communication) It would thus appear that formation of organic hydroperoxides in the radiolysis and photolysis of ethylenic hydrocarbons can be explained via ionic and radical processes.

At low concentrations of oxygen, in aqueous solutions, the usual effects due to oxygen defficiency were observed; the yields of the products per molecule of hydrogen peroxide decomposed were smaller than the corresponding yields in solutions containing high oxygen concentration. On prolonged photolysis, the solutions turned foggy and frothy indicating the formation of polymeric compounds. These experiments also demonstrated that a three fold increase in the ethylene concentration did not induce any chain reaction as far as the formation of oxygenated products was concerned.

At relatively higher oxygen concentrations, the formaldehyde yields were higher than those of any other product. Reaction (59) explains the observed oxygen effect but no exaustive tests were made to check the validity of the proposed mechanism.

Although it is a major product in radiolysis, it is interesting that acetaldehyde was not a product under the conditions of photolysis. Some experiments were made with water decomposing radiations (1850 A^{o}) in solutions not containing hydrogen peroxide. Recent work has shown that (H_2O ---> H + OH) is the major process in water irradiated with this wavelength (Sokolov and Stein 1966). Acetaldehyde was detected under these conditions and indeed was the major product along with formaldehyde. Hydroxyethanal was the next major product and formic acid an organic hydroperoxide (almost certainly hydroxy ethyl hydroperoxide) and hydrogen peroxide were all formed in small quantities. These experiments indicated that hydrogen atoms were, at some stage, essential for the formation of acetaldehyde.

The appearance of hydrogen peroxide in these experiments is of interest. It cannot be produced by pairwise recombination of hydroxyl radicals in photolysed water. It is suggested that this residual hydrogen peroxide (some of it is inevitably decomposed by the U-V light) is produced by reactions of both organic and inorganic peroxy radicals (57) and (7). These experiments were of purely qualitative interest and it was not known to what extent the products were formed as a result of direct absorption of energy.

The intermediate formation of hydroxy ethyl peroxy radicals has been assumed to explain the formation of observed products and it can be seen that a reasonably satisfactory qualitative explanation of the product formation can be made on this basis.

The formation of vinyl radicals by OH abstraction (Cullis, Francis and Swallow 1965) of ethylene would not appear to be a major process under these conditions.

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Appendix 1

Radiolysis of Ethane-Oxygen Aqueous Solutions.

*Ethanol dose-yield table (pH 1.2 radiolysis).

Dose e V x 10^{21}/L	Yield M x 10^{-5} /L
1.02	0.50
2.04	1.60
3.25	1.75
3.50	3.0 0

Nitrite dose-yield table.

0.76	1.55
1.17	2.0 0
1.43	2.52
2.15	4.52
3.25	7.0 0

---

* ethanol determinations could be in error of 50 %

Appendix 1 A

Radiolysis of Ethane-Oxygen Aqueous Solutions.

*
Ethyl hydroperoxide dose-yield table for electron scavenging experiments.

Dose eV x 10^{-21} /L	Yield M x 10^{5} /L	
	N_2O	H_2O_2
0.51	0.20	0.21
1.02	0.18	1.14
1.53	0.36	1.85
2.04	0.38	2.30
2.55	0.70	1.90
3.06	0.70	1.90

* ethyl hydroperoxide determinations could be in error of about 50 % .

Appendix 2

Radiolysis of Methane-Oxygen Aqueous Solutions.

Effect of dissolved nitrous oxide:

Dose eV x 10^{21}/L	Yield M x 10^{5}/L		
At normal gas pressures.			
	HCHO	CH_3OOH	H_2O_2
0.50	1.00	0.21	2.20
1.08	1.30	0.50	4.40
1.58	1.60	0.76	5.25
2.16	1.90	0.95	8.90
3.24	2.10	1.44	13.00
At high gas pressures.			
0.55	1.70	1.13	2.17
1.10	3.10	1.88	4.72
1.65	4.60	3.00	6.55
2.20	6.30	5.35	7.65
2.75	6.40	4.60	10.60
3.30	6.60	6.20	13.00

Appendix 3

Radiolysis of Methane-Oxygen Aqueous Solutions.

Effect of dissolved hydrogen:

Dose eV x 10^{-21}/L	Yield M x 10^{5}/L		
	HCHO	CH_3OOH	H_2O_2
0.55	0.20	1.46	2.06
1.10	0.60	2.41	4.54
1.65	1.10	3.32	6.60
2.20	1.80	4.35	9.35
2.75	2.00	5.10	10.90
3.30	2.70	6.80	13.20

Appendix 4

Radiolysis of Methane-Oxygen Aqueous Solutions.

Effect of oxygen concentration on the yields of products:

Total dose for all irradiations = 1.1×10^{-21} eV /L

O_2 Pressure over aqueous solution	Yield M x 10^5/L	
p.s.i.	HCHO	H_2O_2
20	1.7	6.6
30	1.7	6.4
40	1.7	6.5
50	1.9	7.0
60	1.9	7.8
70	1.8	7.3
80	1.7	7.0
90	1.6	6.9

Appendix 5

Kinetic data for organic peroxides at room temp.

*
Ethyl hydroperoxide(synthetic) t 1/2 = 63 minutes.

Organic hydroperoxide formed in the radiolysis of ethane-oxygen aqueous solutions,

t 1/2 = 62 minutes ,

\+
Hydroxy ethyl hydroperoxide formed in the photolysis of ethylene-oxygen aqueous solutions,

t 1/2 = 9.5 minutes .

*
Methyl hydroperoxide (synthetic)

t 1/2 = 53 and 45 minutes.

Organic peroxide formed in the radiolysis of methane-oxygen aqueous solutions,

t 1/2 = 48 and 53 minutes .

* see Fig 17

\+ see Fig 18

Appendix 6

Decomposition of Methyl Hydroperoxide with Chromotropic Acid Reagent .

Methyl hydroperoxide (synthetic)

CH_3OOH (decomposed) M x 10^{-5}	HCHO (produced) M x 10^{-5}	$\frac{(CH_3OOH)}{(HCHO)}$
3.84	2.06	1.69
6.50	4.14	1.57
11.70	7.45	1.57
11.30	7.05	1.60
Organic peroxide isolated from irradiated methane-oxygen aqueous solutions,		
10.80	6.85	1.58
5.40	3.47	1.55
3.66	2.60	1.41
5.80	3.68	1.58

Appendix 7

Factors for converting observed optical density into concentration.

These factors apply only if the procedure employed is the same as described in the experimental section of this report.

Formaldehyde (D.N.P.H method) = 1.0 x 10^4

Formaldehyde (Chromotropic Acid Method) = 0.7 x 10^4

Acetaldehyde = 0.69 x 10^4

Hydroxyethanal = 0.687 x 10^4

Formic Acid = 0.583 x 10^3

Hydrogen peroxide and Organic peroxides by Iodide Method = 1.15 x 10^4

Hydrogen peroxide by Titanium Sulphate Method = 2.45 x 10^3

Nitrite = 4.0 x 10^5

Appendix 8

Specifications for Perkin Elmer Gas Chromatograph.

Stainless steel column (2 x 1/4 inch O.D).

Packing- Polyethylene glycol on Chromosorb P.

60 to 80 mesh.

Operating temperature = 80° C.

Flow rate of carrier gas (Argon) = 50 ml Min^{-1}.

Operating voltage for flame ionization detector

= 200 v.

Flow system adjusted to pass maximum amount of injected sample through the detector chamber.

Appendix 9

Photolysis of Hydrogen Peroxide Solutions containing 5.5×10^{-3} M Allyl Alcohol.

H_2O_2 M x 10^5/L			
Initial	Final	H_2O_2 (decomposed)	Time Min
20.60	4.58	16.02	45
20.50	3.48	16.66	60
20.10	3.90	16.20	90
20.30	4.00	16.30	75
25.00	9.00	16.00	45
24.80	8.00	16.80	60
25.10	8.50	16.60	75
18.00	4.08	13.92	90
17.80	5.72	12.08	60
17.90	5.90	12.00	45
18.00	6.20	11.80	45

Appendix 10

Rat of decomposition of hydrogen peroxide.

	H_2O_2 decomposition M x 10^5		
Time	Allyl alcohol A	ethylene-oxygen B	$\frac{A}{B}$
at pH 5.5			
45	16.02	12.70	1.25
45	16.02	12.20	1.30
45	11.80	8.17	1.40
45	12.00	9.00	1.30
45	16.00	14.50	1.15
at pH 2.0			
45	11.80	7.80	1.50
60	16.30	10.00	1.63
60	16.66	9.05	1.85
90	16.20	9.10	1.78
75	16.30	9.00	1.80