A THESIS

entitled

STUDIES OF THE RADIATION - INDUCED OXIDATION OF ORGANIC COMPOUNDS

submitted by

JOHN MICHAEL FRANCIS

for the Degree of Doctor of Philosophy

in the University of London

ABSTRACT

This thesis describes a detailed investigation of the radiation-induced oxidation of ethylene in aqueous solution at ambient temperatures and under gas pressures of from 5 to 40 atmospheres.

In Section I, previous work on the radiation-induced oxidation of organic compounds is discussed alongside the results of autoxidation studies carried out with the corresponding classes of compounds. Comparison of the two types of reaction shows several points of interest attaching to the oxidation of olefins.

Section II describes the apparatus constructed for the preparation and handling of solutions of ethylene-oxygen mixtures at high pressures. An account is also given of the procedure used in carrying out the radiolysis, and of the specially sensitive methods for the identification and estimation of the products formed, many of which are only present in very low concentration.

The results presented in Section III relate to the gamma-radiolysis of ethylene and ethylene-oxygen solutions, and the influence on the products of dose, reactant gas pressures, pH of the solution and additives has been systematically investigated. In the absence of oxygen, polymerisation (to yield what is essentially polyethylene) is the main process, although smaller amounts of hydrogen peroxide and of C_2 - C_4 aldehydes are formed simultaneously. The

rate constant for the reaction of the solvated electron with ethylene has been determined directly by a pulse radiolysis technique. In the presence of oxygen, polymerisation is inhibited and quite a variety of oxygenated organic products are formed; these include formaldehyde, acetaldehyde, and propionaldehyde. An important stage in the reaction appears to be the formation of the β-hydroxyethylhydroperoxy radical, some evidence for which has been obtained during pulse radiolysis experiments. In addition, the organic peroxide, which is formed in the irradiated solutions simultaneously with hydrogen peroxide, has been tentatively identified as β-hydroxyethylhydroperoxide.

Finally, in Section IV, the probable reaction paths of the various radical and ionic species formed during the radiolysis are discussed in relation to the experimental measurements recorded in the previous Section. The initial reaction in both the oxygen-free and oxygen-containing systems appears to involve addition of the primary species formed from water to the solute ethylene molecules. Reaction schemes involving secondary reactions of the initial species so formed are suggested to account for the formation of the oxidation products observed.

ACKNOWLEDGMENTS

It is a pleasure to thank Dr. C. F. Cullis and Dr. A. J. Swallow for their supervision, guidance and encouragement throughout the present work.

In addition, the author would like to thank Prof. D. M. Newitt and Drs. J. H. Burgoyne and K. E. Bett for their advice relating to the high pressure experiments.

The author is also grateful to Dr. J. P. Keene and other staff of the Christie Hospital and Holt Radium Institute, Manchester, for the necessary facilities to carry out the pulse radiolysis experiments.

Grateful acknowledgment is made for the award of a D.S.I.R. Research Studentship for the period 1960-63.

Finally, the author wishes to thank Mr. G. R. Hall and his colleagues in the Nuclear Technology Laboratory for providing a congenial atmosphere in which to work.

Department of Chemical Engineering
and Chemical Technology,
Imperial College,
London, S.W.7.

July, 1963.

CONTENTS

		Page
	ABSTRACT	2
	ACKNOWLEDGMENTS	4
SECTION I.	THE RADIATION-INDUCED OXIDATION AND AUTOXIDATION OF ORGANIC COMPOUNDS	6
SECTION II.	EXPERIMENTAL	52
SECTION III.	RESULTS	131
SECTION IV.	DISCUSSION	192
	BIBLIOGRAPHY	221

SECTION I

THE RADIATION-INDUCED OXIDATION AND THE AUTOXIDATION OF ORGANIC COMPOUNDS

CONTENTS

		Page
A.	Introduction	9
B.	Radiation-induced Oxidation	12
1.	Irradiation of water and aqueous solutions	13
2.	The role of molecular oxygen in radiation-induced reactions	16
3.	Aliphatic compounds	
(a)	Saturated hydrocarbons	18
(b)	Unsaturated hydrocarbons	23
(c)	Ethers	26
(d)	Alcohols	28
(e)	Aldehydes and Ketones	30
(f)	Carboxylic acids	30
(g)	Esters	33
4.	Aromatic compounds	34
5.	Polymers	36
C.	Autoxidation	38
1.	Aliphatic compounds	
(a)	Saturated hydrocarbons	39
(b)	Unsaturated hydrocarbons	42
(c)	Ethers and Alcohols	44
(d)	Aldehydes	45
(e)	Ketones and Enols	45

		Page
C.	Autoxidation (continued)	
2.	Aromatic compounds	46
3.	Polymers	47
D.	The Present Research	
1.	Previous work on the ethylene--oxygen system	48
2.	General aims of the current work	50

A. Introduction

The interaction of high energy radiation with the molecules of an irradiated medium results in the production of electronically excited or ionized molecules. There are several possible secondary processes which may follow the formation of the primary ions and excited molecules, and which occur before any irreversible chemical change takes place. These may include transfer of excitation and ionization energy between like and unlike molecules, neutralization of ions, and formation of negative ions, all with or without decomposition to radicals or molecules, and also the breakdown of excited molecules to other radicals or molecules.

The observed chemical effects which follow are usually the result of combination of the free radicals with each other or of reaction with other species present in the medium, their fate being largely determined by their proximity to each other and by the activation energies of the various competing reactions. Ion-molecule interactions are also recognised to be important in determining the possible reaction path.

In general, organic molecules which have acquired sufficiently enhanced chemical activity due, for example, to an increase in temperature, the presence of a catalyst,

or absorption of light, react readily with molecular oxygen. For this reason, it is well established that when oxygen is present the essential intermediates are often formed by the direct addition of molecular oxygen to free radicals.

The data available from oxidation systems have demonstrated the importance of peroxy-radical intermediates in determining the reaction path. The subsequent reactions of these peroxy-radicals with molecules or with other radicals, or their isomerization or decomposition then lead ultimately to the final oxidation products. The role of free-radical intermediates of this type has already become an accepted stage in the oxidation of hydrocarbons initiated by means other than radiation. In fact, the most direct line of comparison has been drawn between the radiation-induced oxidation and the autoxidation of liquid hydrocarbons. It is of general interest, therefore, to extend this comparison to the liquid phase oxidation of other classes of organic compounds. The formation and decomposition of different classes of organic peroxides have already been freely discussed in relation to the various autoxidation processes [1, 2]. These reactions probably also play an important part in radiation-induced oxidation.

Such radiation-induced oxidation processes are of

general occurrence and involve both very reactive and exceedingly stable organic compounds. They do not involve direct action of the radiation on oxygen and are therefore observed even at very low oxygen concentrations. With more oxygen present, the oxygen molecule may itself interact with the radiation and become ionized, excited or dissociated. This may lead to new paths for the reaction of oxygen with organic compounds.

It was at one time thought that the large scale use of ionizing radiation might be potentially attractive for preparing products of commercial importance. Its use would, however, be confined to exothermic reactions in which the radiation serves to initiate long reaction chains, such as the oxidation of hydrocarbons. The studies which have been made both with gaseous and liquid saturated hydrocarbons and oxygen, and with saturated hydrocarbon gases in aqueous solution, have clearly indicated, however, that under the conditions so far employed the oxidation initiated by gamma rays almost invariably gives a very poor yield of product for a given energy expenditure.

Comparison shows that the products of radiation-induced and thermal oxidation are generally similar, e.g., peroxides, carbonyl compounds, alcohols, acids, etc. It is proposed, therefore, first to examine the nature

of oxidation processes due to ionizing radiation, and then later in this Section, to discuss the various autoxidation reactions which occur with the same classes of organic compounds.

B. Radiation-induced Oxidation

The overall influence of oxygen, especially with the less densely ionizing radiations, e.g., gamma-rays or fast electrons, is one of the most striking effects in radiation chemistry. Owing to the limited solubility of oxygen, it is often found that oxidation predominates in the early stages of an irradiation, and is then replaced by the normal oxygen-free reaction after all the oxygen initially present has been consumed. It is important, therefore, with inhomogeneous fields of irradiation, to ensure that oxygen is not exhausted locally in the solution.

Small quantities of impurities can exert a powerful influence on radiation-induced reactions, and one such important 'impurity' in many instances is oxygen. Efficient deaeration of liquids prior to irradiation is thus an absolute criterion for all work carried out in the absence of oxygen.

The chemical species formed by radiation are sometimes unstable and may continue to react long after the irradiation has been stopped. This is particularly

noticeable when oxygen is present during irradiation, reactive compounds such as peroxides often being formed.

1. Irradiation of water and aqueous solutions

Considerable interest has centred around the chemical action of ionizing radiation on aqueous systems[3]. In 1944, Weiss [4] suggested that the most important primary process is the formation of hydrogen atoms and hydroxyl radicals according to the net process:

$$H_2O \longrightarrow H + OH$$

This simple equation has remained the basis for the present understanding of the radiation chemistry of water, including oxygen effects and the radiation-induced formation of peroxidic compounds in aqueous systems.

Establishment of the concept of 'molecular' and 'radical' yields in the radiolysis of water by Allen, et al.[5], together with the radical diffusion model, led to an understanding of the effects of scavenging solutes.

The basis of the radical diffusion model is that the hydrogen atoms and hydroxyl radicals formed during irradiation of water are produced either in localised clusters ('spurs') or in tracks, so that initially they tend to combine in pairs to form the 'molecular' products, hydrogen, hydrogen peroxide and water. The probability of such combination diminishes rapidly as the radicals diffuse away, so that there is a sharp distinction

between the 'molecular' products, and the free radicals which escape this combination by diffusion, or by reaction with added solutes. For energetic gamma-rays and electrons, the primary events occur in widely separated spurs (ca. 20Å radius) which will lie in the region of 5000Å apart. Under conditions of high linear energy transfer (LET), the spurs overlap and the track becomes columnar; the molecular yield is then found to increase at the expense of the radical yield.

To a first approximation, molecular and radical yields are constant for a given type of radiation at low scavenging solute concentrations. With increasing solute concentration, however, radical combination within the track diminishes, so that the yield of molecular products should decrease slowly.

It is apparent that the chemical effect on water in both low and high LET systems is much the same, the chief difference between them lying in the geometrical distribution on the molecular scale of the energy imparted to the water. The non-uniform distribution in concentration of reactive intermediates is one of the chief distinguishing characteristics of radiation chemistry.

Many proposed mechanisms in the radiolysis of aqueous solutions employ the radicals H and OH as the only intermediates of chemical importance formed from

water. It is clear that the situation is actually much more complicated, and much speculation exists about other entities that may be present and about their possible roles. At various times, almost all intermediates of the possible types $(H_aO_b)^{\pm}_c$ have been proposed (where a, b and c, are either zero or a positive integer). A real advance was made by Barr and Allen[6], who stated that two kinds of reducing entities are formed. Recently it has become clear that the principal reducing agent in neutral water is in fact the solvated electron[7,8,9]. In acid solutions the solvated electron is converted into a normal hydrogen atom by reaction with hydrogen ions according to the equation:

$$e^-_{aq} + H^+_{aq} \longrightarrow H_{aq}$$

There is also considerable evidence that the species H_2^+ may exist in highly acid solutions[10,11]. Similarly the radical OH might conceivably exist in its basic form O^- or in its acidic form H_2O^+ [12,13]. In accordance with current theory relating to the solvated electron, the latter species is presumably formed simultaneously in the reaction:

$$H_2O \longrightarrow H_2O^+ + e^-_{aq}$$

The H_2O^+ ion then undergoes a further fast reaction resulting in the formation of a hydroxyl radical:

$$H_2O^+ + H_2O \longrightarrow H_3O^+ + OH$$

It must be concluded therefore that, although the free radicals are often written as H and OH, their actual molecular constitution is not necessarily so simple.

2. The role of molecular oxygen in radiation-induced reactions

In the case of organic solutes, the influence of oxygen on the oxidation yield may depend on a number of factors. Firstly it can react rapidly with the hydrogen atoms produced by the radiation:

$$H + O_2 \longrightarrow HO_2 \quad (1)$$

Secondly, the initial reaction of OH radicals with a solute, RH, can in many cases be represented as a dehydrogenation step of the form

$$RH + OH \longrightarrow R + H_2O \quad (2)$$

In the absence of dissolved oxygen, the free radicals, R, could then react according to equations (3) to (5), where X may be, for example, a H atom:

$$R + X \longrightarrow RX \quad (3)$$

$$2R \longrightarrow R_2 \quad (4)$$

$$2R \longrightarrow RH + \text{olefin} \quad (5)$$

Molecular oxygen will influence the course of the radiolysis as a result of its interaction with the radicals:

$$R + O_2 \longrightarrow RO_2 \quad (6)$$

and/or

$$R + O_2 \longrightarrow \text{olefin} + HO_2 \quad (7)$$

In this manner, reactions (3) to (5) can be suppressed.

It has been suggested[14] that HO_2 radicals are less powerful oxidising agents than OH radicals, and that they are relatively unreactive, particularly towards saturated organic molecules. On purely thermodynamic grounds, this is to be expected since the bond dissociation energy of water D (H-OH) is 118 kcal.mole^{-1}, whereas the bond dissociation energy of hydrogen peroxide D ($H-O_2H$) is approximately 90 kcal.mole^{-1},[15]. It has also been suggested[14] that particularly in neutral solutions, the perhydroxyl radical may act as a reducing agent in the form of its anion, O_2^-, due to the dissociative equilibrium:

$$HO_2 \rightleftharpoons H^+ + O_2^-$$

It has been shown that in most cases, the HO_2 radicals react with an organic peroxy radical, e.g., in the irradiation of aqueous ethanol solutions[16],

$$CH_3\underset{\underset{OO}{|}}{C}HOH + HO_2 \longrightarrow CH_3CHO + H_2O_2 + O_2$$

and/or disproportionate to form hydrogen peroxide,

$$2\ HO_2 \longrightarrow H_2O_2 + O_2$$

An important feature of the intervention of oxygen in radiation-induced reactions is that once the molecular

oxygen has reacted with an organic radical to form RO_2, there is no possibility of reforming the parent compound RH.

3. Aliphatic compounds

(a) Saturated hydrocarbons

Early work[17] has shown that irradiation of liquid hydrocarbons, saturated with oxygen at atmospheric pressure, leads to the formation of peroxides, carbonyl compounds, alcohols, acids, etc. A characteristic feature of these processes is that at room temperature all the other products are formed simultaneously with peroxides from the beginning of irradiation[18, 19, 20]. This is in contrast to autoxidation processes where the other products clearly arise from further reaction of the initially formed peroxides.

Autoxidation reactions are currently assumed to be chain reactions, hydroperoxide being formed according to reactions (1) to (3), and being subsequently converted into carbonyl compounds, and finally into acids.

$$RH \longrightarrow R + H \qquad (1)$$

$$R + O_2 \longrightarrow RO_2 \qquad (2)$$

$$RO_2 + RH \longrightarrow ROOH + R \qquad (3)$$

In the case of saturated hydrocarbons, such processes start to occur at temperatures above 100°C.

The direct effect of radiation on the RH molecule

results in the production of an R radical according to the primary process

$$RH \longrightarrow R + H$$

The R radical produced in this latter reaction again combines with molecular oxygen to form an RO_2 radical. The reason why the radiation-induced oxidation is not a chain reaction is probably that at the high dose rates used, the RO_2 radicals do not abstract hydrogen from other organic molecules, according to reaction (3), but preferentially react with one another. No other radical is formed as a result of this mutual interaction so that the possibility of chain-propagation is eliminated.

The simultaneous appearance of all the products observed must be due, therefore, to parallel conversion paths of the same primary radicals, or to the simultaneous reactions of different primary radicals. The general mechanism includes in addition to reactions (2) and (3) the following possible reaction paths, where R', R'' and R''' may be hydrocarbon radicals or hydrogen atoms:

$$R'R''R'''CO_2 \longrightarrow R'R''C(O\text{-}OR''') \longrightarrow R'R''CO + OR''' \qquad (4)$$

$$OR + RH \longrightarrow ROH + R \qquad (5)$$

$$R'O_2 + R'' \longrightarrow R'OOR'' \qquad (6)$$

$$R'O_2 + R''O_2 \longrightarrow R'OOR'' + O_2 \qquad (7)$$

Thus the peroxy radical RO_2 may react with hydrocarbon

molecules abstracting hydrogen atoms and forming a hydroperoxide, react with another radical forming a disubstituted peroxide, or isomerise and dissociate, forming carbonyl compounds and alkoxy radicals.

Reactions (4) and (5) require a finite activation energy but reaction (7) does not. The assumption has been made that, when reactions occur during radiation-induced oxidation at room temperature, excess energy must be present in the peroxy radicals[18]. It is not possible for chain mechanisms to develop under these conditions, as stated previously, since, for example, the radical R from reaction (3) may form a peroxy radical RO_2, but may no longer have the energy necessary to repeat reaction (3). The relatively low yields of oxidation products at room temperature are thus determined by the number of high energy primary radicals formed by irradiation.

The following sequence of reactions has been suggested to account for the formation of alcohols and carbonyl compounds during the radiation-induced oxidation of cyclohexane[21].

$$\text{cyclo-}C_6H_{12} \longrightarrow \text{cyclo-}C_6H_{11} + H \qquad (8)$$

$$\text{cyclo-}C_6H_{11} + O_2 \longrightarrow \text{cyclo-}C_6H_{11}O_2 \qquad (9)$$

$$2\ \text{cyclo-}C_6H_{11}O_2 \longrightarrow \text{cyclo-}C_6H_{11}OH + \text{cyclo-}C_6H_{10}O + O_2 \qquad (10)$$

The formation of the cyclohexylperoxy radical in the

cyclohexane-oxygen system has already been established from pulse radiolysis studies, and the activation energy for reaction (10) has been shown to be 1 kcal.mole^{-1},[22]. However, even at the highest concentrations of scavenger, a limiting value of the ketone yield was obtained[21]. This suggests that an additional process involving non-radical intermediates may be occurring, e.g., an excited-molecule reaction,

$$\text{cyclo-}C_6H_{12}^{*} + O_2 \longrightarrow \text{cyclo-}C_6H_{10}O + H_2O \quad (11)$$

It is not possible to distinguish between this reaction and the formation of an intermediate cyclohexylhydroperoxide, which would then decompose to ketone.

In general, at temperatures above about 100°C, the oxidation yields increase markedly and the reaction becomes a free-radical chain reaction resembling that occurring in the normal autoxidation of hydrocarbons [23,24]. Emanuel et al.[25] have reported on the initiation at elevated temperatures of the chain oxidation of isodecane. The non-initiated oxidation reaction at 120° had an induction period of ca.20hr. The rate of chain initiation, w_o, calculated from the thermal reaction of isodecane with oxygen, was 10^2 - 10^3 radicals. ml^{-1}.sec.$^{-1}$; under irradiation conditions during the initial stages of the reaction, w_o was 10^{12} radicals. ml^{-1}.sec.$^{-1}$ In the latter case, the curve

had a sharply developed autocatalytic shape, and the maximum velocity was over ten times greater than for the non-initiated reaction. At still higher temperatures, where combustion is occurring, oxidation is already proceeding so fast that radiation, even at very high dose rates, can produce only a very slight effect on the reaction[26, 27].

In view of the possible importance of organic hydroperoxides and peroxides in the radiolytic oxidation of organic compounds, it is perhaps surprising that the formation of these compounds has not been investigated in more detail. The first system where a relatively stable hydroperoxide was detected among the products formed was a neutral aqueous solution of methane[28]. Prior to this, little work had been done with solutions of saturated hydrocarbons probably on account of their low solubility. Apart from methyl hydroperoxide, the other major products were hydrogen peroxide and formaldehyde. It was suggested that the organic peroxide was formed according to equations (12) to (14) as a result of the addition of oxygen to methyl radicals:

$$CH_4 + OH \longrightarrow CH_3 + H_2O \qquad (12)$$

$$CH_3 + O_2 \longrightarrow CH_3OO \qquad (13)$$

$$CH_3OO \xrightarrow{\text{(reduction)}} CH_3OOH \qquad (14)$$

The reducing agent effective in reaction (14) might be

methane, hydrogen peroxide or a perhydroxyl radical. In view of the observed dependence on pH, this reduction process is probably brought about[14] by the anion of the perhydroxyl radical, O_2^-, as in equations (15) and (16).

$$CH_3OO + O_2^- \longrightarrow CH_3OO^- + O_2 \quad (15)$$

$$CH_3OO^- + H^+ \rightleftharpoons CH_3OOH \quad (16)$$

The low yield of organic peroxides indicates that reaction[14] is slow, and that most of the methyl peroxy radicals disappear in some other way.

The only other work on saturated hydrocarbons in aqueous solution has been concerned with solutions of cyclohexane[29]. The hydrogen yield obtained in this system indicates that in the absence of oxygen all the hydrogen atoms react with cyclohexane by hydrogen abstraction. It may be generally expected, therefore, that both hydrogen atoms and hydroxyl radicals will abstract hydrogen atoms from saturated hydrocarbon molecules in aqueous solution.

(b) Unsaturated hydrocarbons

Since the present research is principally concerned with the radiation-induced oxidation of ethylene in aqueous solution, this system will be fully discussed later in the present Section. At this point, it is appropriate to review the radiation chemistry of other unsaturated hydrocarbons in the presence of oxygen.

The oxidation of cyclohexene has been studied in the liquid phase under X-ray irradiation[30]. The reaction is not initiated by peroxide decomposition, since all the oxygen consumed can be recovered exclusively as the peroxide product.

However, the gamma-irradiation of aqueous solutions of unsaturated hydrocarbons probably results in the addition of hydrogen atoms and hydroxyl radicals to the double bond rather than the abstraction of hydrogen atoms. When aqueous solutions of propylene-oxygen gas mixtures are irradiated, the main product is a hydroperoxide formed in comparatively high yield[31]. The total aldehyde yield in this instance is made up of much smaller quantities of formaldehyde, acetaldehyde and propionaldehyde. In addition, formic acid is produced during the radiolysis together with hydrogen peroxide. It was presumed that a hydroxyhydroperoxide is formed according to the reaction sequence:

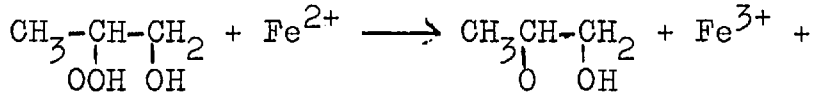
$$CH_3-CH=CH_2 + OH \longrightarrow CH_3-\underset{\displaystyle OH}{CH}-CH_2 \qquad (1)$$

$$CH_3-\underset{\displaystyle OH}{CH}-CH_2 + O_2 \longrightarrow CH_3-\underset{\displaystyle OO}{CH}-\underset{\displaystyle OH}{CH_2} \qquad (2)$$

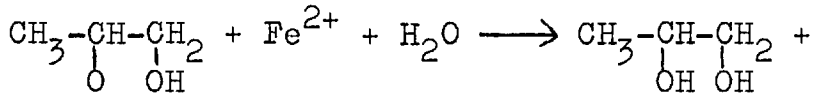
$$CH_3-\underset{\displaystyle OO}{CH}-\underset{\displaystyle OH}{CH_2} \xrightarrow{\text{(reduction)}} CH_3-\underset{\displaystyle O_2H}{CH}-\underset{\displaystyle OH}{CH} \qquad (3)$$

Some experimental support follows from the observation that, on treatment of the irradiated solution with an

excess of ferrous salt, two ferric ions are produced per hydroperoxide group decomposed, and propylene glycol is formed. This process can best be represented by equations (4) and (5):



(4)



(5)

It can thus be stated that in general the action of ionizing radiation on olefinic systems in the presence of oxygen may give rise to more or less stable hydroxy-hydroperoxides[32].

Weiss and co-workers irradiated acetylene in aqueous solution in the absence and in the presence of oxygen[33]. In the absence of oxygen, they obtained a yellow-white solid polymer and several different aldehydes such as formaldehyde, acetaldehyde and crotonaldehyde. Glycolaldehyde was also produced but the yields were irreproducible. In the presence of oxygen, the main products were glyoxal and hydrogen peroxide. The yield of peroxide was found to be independent of pH and of the concentrations of both acetylene and oxygen. However, the much higher yield of glyoxal was strongly dependent on both pH and the concentrations of the reactants. The glyoxal formation was thus ascribed to a chain reaction

in which the chains are short. The exact nature of the chain carriers was not clear, but the following mechanism was suggested:

$$CH\equiv CH + OH \longrightarrow (HO)\,CH{=}CH \qquad (6)$$

$$(HO)CH{=}CH + O_2 \longrightarrow (HO)\,CH{=}CHOO \qquad (7)$$

$$(HO)CH{=}CHOO \longrightarrow CHO.CHO + OH \qquad (8)$$

These results suggest that the chain may appear quite suddenly with variation of the relative concentrations of acetylene and oxygen in the solution.

(c) Ethers

A comparison of the yields of different products formed during the radiation-induced oxidation of iso-propyl ether has shown that these are formed in two ways[18]. High yields are obtained both for the peroxide products, probably ether hydroperoxides, and for the carbonyl compounds (formaldehyde, acetaldehyde, acetone and a long chain methyl ketone). All these products are probably the result of chain reactions, whereas the alcohols and acids are formed in non-chain processes in much lower yields.

In the presence of oxygen, the principal products again appear to arise from the addition of molecular oxygen to radicals:

$$(CH_3)_2\dot{C}\text{-}OCH(CH_3)_2 + O_2 \longrightarrow (CH_3)_2\underset{\underset{OO\cdot}{|}}{C}\text{-}OCH(CH_3)_2 \qquad (1)$$

Hydroperoxide formation then follows as a result of subsequent hydrogen atom abstraction from another ether molecule. The ensuing radical thus assures the continuation of the chain.

A radical similar to that formed in reaction (1) could also explain the formation of equivalent amounts of alcohol and acid:

$$(CH_3)_2CH.O.\dot{C}HCH_3 + O_2 \longrightarrow (CH_3)_2CH.O.\underset{\underset{OO}{|}}{C}HCH_3 \qquad (2)$$

$$(CH_3)_2CH.O.\underset{\underset{OO}{|}}{C}HCH_3 \longrightarrow (CH_3)_2CHO. + CH_3COOH \qquad (3)$$

$$(CH_3)_2CHO. + RH \longrightarrow (CH_3)_2CHOH + R \qquad (4)$$

In this case, the initial radical $(CH_3)_2CHO\dot{C}HCH_3$ is not regenerated and no chains develop.

The limited data available from the radiation-induced oxidation of di-ethyl ether seem also to indicate definitely the existence of chain processes[18]. The initial yields of peroxide and carbonyl compounds are of the same order of magnitude as those obtained for iso-propyl ether.

The main reaction products from the radiolysis of oxygen-saturated aqueous solutions of iso-propyl ether are acetone, alcohol and hydrogen peroxide.

The only important organic radical is $(CH_3)_2\dot{C}.O.CH(CH_3)_2$, formed by hydrogen abstraction from the ether molecule.

(d) Alcohols

The radiolysis of ethanol is the presence of oxygen may possibly involve short chains at ordinary temperatures[34,35]. The aldehyde and water yields are greater than those obtained in the absence of oxygen; the formation of acids and peroxides is also recorded. The yields in the presence of oxygen are found to be dependent on dose-rate.

When oxygen is present in aqueous solution, the hydrogen atoms form perhydroxyl radicals, and the hydroxyl radicals react with the alcohol to yield peroxy radicals[16],

$$OH + CH_3CH_2OH \longrightarrow CH_3\dot{C}HOH + H_2O \qquad (1)$$

$$CH_3\dot{C}HOH + O_2 \longrightarrow CH_3CHOH \quad (OO) \qquad (2)$$

If the peroxy radical is denoted by AHO_2, the radiolysis may be represented by the following reaction scheme:

$$HO_2 + HO_2 \longrightarrow H_2O_2 + O_2 \qquad (3)$$

$$HO_2 + AHO_2 \longrightarrow A + H_2O_2 + O_2 \qquad (4)$$

$$AHO_2 + AHO_2 \longrightarrow 2A + H_2O_2 + O_2 \qquad (5)$$

Glycol formation is completely suppressed in these solutions. There is also some evidence that acids and

stable organic peroxides are formed as secondary products of the radiolysis[36, 37, 38]; the reaction is not, however, a chain reaction.

The radiation chemistry of de-aerated liquid ethanol, and de-aerated aqueous ethanol solutions, has recently been studied by a pulse radiolysis technique[39]. The spectrum of the transient species obtained in both cases was that of the α-ethanol radical,

$$CH_3\dot{C}HOH \quad .$$

When allyl alcohol is irradiated in aqueous solution at a pH of 1.2 in the presence of oxygen, acraldehyde, glycolaldehyde and formaldehyde are formed in addition to an organic hydroperoxide[31]. Further investigation has shown that the glycolaldehyde and formaldehyde are secondary products formed by decomposition of the organic hydroperoxide during the analytical procedure. From an investigation of the rate of liberation of iodine from iodide by the irradiated solution, it appears that two hydroperoxides are formed. The most obvious route to acraldehyde would involve initial abstraction of hydrogen by the hydroxyl radicals, whereas formation of the hydroperoxides would presumably be initiated by addition of a hydroxyl radical to the double bond. In this instance, the relatively high yields of organic hydroperoxide suggest that, in addition to hydroxyl radicals, hydrogen atoms

and/or perhydroxyl radicals may be capable of adding to the double bond.

(e) Aldehydes and Ketones

In aqueous solution and in the absence of oxygen, formaldehyde, acetaldehyde and propionaldehyde are oxidised to the corresponding acids[40].

Very little work has been reported on the irradiation of ketones in solution. Hydrogen was the only gaseous product obtained from aqueous solutions of acetone irradiated with X-rays in the absence of oxygen[40]; the hydrogen yield was found to decrease at concentrations of acetone greater than 10^{-3}M. Hydrogen peroxide, however, appeared in these solutions, showing that hydrogen atoms react with acetone in preference to hydroxyl radicals. With alcohols, aldehydes or acids, no hydrogen peroxide is found under comparable conditions.

The only other ketone which has been studied in solution is cyclohexanone[41]. This compound was carbonylated in the presence of oxygen to give 1,2- and 1,3- cyclohexanediones. In addition, the ring was broken at the carbonyl group to give adipic acid and a hydroxycaproic acid; both these products were considered to arise from the decomposition of initially formed hydroperoxides.

(f) Carboxylic acids

The mechanism of the radiation-induced

oxidation of formic acid in aqueous solution has been extensively studied by Hart[42], and shows features which are generally regarded as typical for organic compounds irradiated in aqueous solution.

The only products from the gamma-irradiation of millimolar formic acid solutions in the absence of oxygen were found to be hydrogen and carbon dioxide which are formed in equimolar amounts. To explain the experimental results, Hart suggested the following mechanism:

$$H + HCOOH \longrightarrow H_2 + COOH \qquad (1)$$

$$OH + HCOOH \longrightarrow H_2O + COOH \qquad (2)$$

$$2\ COOH \longrightarrow CO_2 + HCOOH \qquad (3)$$

$$COOH + H_2O_2 \longrightarrow H_2O + CO_2 + OH \qquad (4)$$

The addition of hydrogen peroxide to the formic acid system results in a marked acceleration of the rate of production of carbon dioxide. The carbon dioxide yields are thus indicative of a chain reaction, and explain why hydrogen peroxide is not produced in the absence of oxygen.

The decrease in carbon dioxide production with increasing hydrogen peroxide concentration indicates that the chain terminating step involves the hydroxyl radical and hydrogen peroxide,

$$OH + H_2O_2 \longrightarrow H_2O + HO_2 \qquad (5)$$

In contrast to the marked increase in the rate of carbon dioxide production with concentration of added hydrogen

peroxide, hydrogen production remains substantially constant until after the maximum rate of carbon dioxide production has been reached. Thereafter a gradual decrease in hydrogen production occurs. This drop in yield was suggested to be due to the competition between the reaction of hydrogen atoms with hydrogen peroxide according to:

$$H + H_2O_2 \longrightarrow H_2O + OH \quad (6)$$

and reaction (1).

The gamma-irradiation of aqueous formic acid solutions in the presence of oxygen has also been studied by Hart [43,44]. Under these conditions, the hydrogen atoms react with oxygen in preference to formic acid,

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

and their chain propagation is terminated by

$$COOH + O_2 \longrightarrow CO_2 + HO_2 \quad (8)$$

The perhydroxyl radicals are removed by

$$HO_2 + HO_2 \longrightarrow H_2O_2 + O_2 \quad (9)$$

This explains the inhibiting action of oxygen on the formation of carbon dioxide in the irradiation of formic acid solutions containing hydrogen peroxide.

The yield of hydrogen decreases and that of peroxide increases as the oxygen concentration is increased in the formic acid solution, and at sufficiently high oxygen concentrations, only the molecular hydrogen

yield from water radiolysis is obtained. When the concentration of formic acid is increased, the hydrogen yield decreases, instead of increasing according to the above mechanism. It was suggested that at high concentrations of formic acid, electron capture by formic acid is competing with electron capture by water [45,46,47]. The following processes were then postulated:

$$H_2O \longrightarrow H_2O^+ + e \qquad (10)$$

$$H_2O^+ \longrightarrow H^+ + OH \qquad (11)$$

$$H_2O + e \longrightarrow H_2O^- \qquad (12)$$

$$HCOOH + e \longrightarrow HCOOH^- \qquad (13)$$

$$H_2O^- \longrightarrow H + OH^- \qquad (14)$$

$$HCOOH^- \longrightarrow HCO + OH^- \qquad (15)$$

In view of the competition for electrons between reactions (12) and (13), fewer hydrogen atoms are produced in reaction (14), thus leading to the reduction of the hydrogen yield. The formyl radical, HCO, must lead to a product other than hydrogen. In fact, carbon monoxide has been detected in the solutions at high concentrations of formic acid.

(g) Esters

Esters, especially unsaturated esters, become oxidised on irradiation when oxygen is present, and the final products include acids identical with those produced by normal antoxidation [48], and carbonyl

compounds [49]. Hydroperoxides derived from the free radicals produced by irradiation are important primary products, and their formation depends strongly on conditions. The nature of the peroxides is also similar to that of the hydroperoxides produced by autoxidation. Even at very low temperatures, the free radicals produced by irradiation can react with oxygen to give in the first instance peroxy radicals.

4. Aromatic compounds

The oxidation of liquid aromatic hydrocarbons resembles that of aliphatic compounds. The reaction is not, however, a chain reaction, except at very low dose rates (up to 350 rads/min.) Under the latter conditions, the reaction resembles photochemical oxidation except for the obvious difference in initiation [50]. The first products of the radiation-induced oxidation appear to be organic peroxides and hydroperoxides, hydrogen peroxide and carbonyl compounds.

Irradiation of benzene in the presence of oxygen produces phenol. Toluene, on the other hand, after prolonged irradiation at a low dose rate, yields benzaldehyde as the main product, as well as benzoic and formic acids. Among other aromatic compounds which have been irradiated at low dose-rates in the presence of oxygen, the oxidation of benzyl alcohol has been

reported to give yields clearly indicative of a chain reaction. The increased activity is, therefore, attributed to the hydrogen atoms of the - CH_2OH group.

The results of the irradiation of aqueous solutions of aromatic compounds are explicable in terms of free radical reactions. The fact that 'energy transfer' mechanisms, involving interaction between ionized or excited water molecules and the solute are not considered to play an important role is probably due to the very low concentrations involved [50].

Irradiation of saturated de-aerated aqueous benzene solutions yields phenol and diphenyl [29,51] although the identification of the latter compound has been questioned[52]. Ultra-violet absorption spectra of some of the transient species were recorded by synchronised flash absorption spectroscopy [53]. On the basis of both spectrographic and kinetic evidence, it was concluded that the hydroxyl radical enters the ring, and the spectrum was assigned to the hydroxycyclohexadienyl radical, (OH) C_6H_6.

In aerated solutions, the main products are phenol and hydrogen peroxide. A further transient species detected by the pulse radiolysis technique in these solutions is the peroxy radical, $(OH)C_6H_6OO$ [53]. An additional aldehydic product is formed with small yield

in the aerated solutions, and has been identified as mucondialdehyde [54,55]. Due to the absence of diphenyl in the aerated solutions, ring opening and resulting formation of the dialdehyde may well occur via the reaction,

$$C_6H_5 + O_2 \longrightarrow C_6H_5OO$$

The irradiation of aerated aqueous solutions of other aromatic compounds indicates the probable point of free-radical attack. Mono-substituted benzenes, for example, are hydroxylated at all three possible positions in the ring, together with attack at the side-group.

When phenol is irradiated in aqueous solution either in the presence or the absence of oxygen, it is found to be not very reactive towards hydroxyl radicals [56]. However, the products are chiefly the ortho and para-dihydroxybenzenes. In acid solutions, o-benzoquinone is formed as a primary product, probably from the action of a perhydroxyl radical on a 'phenol radical'.

5. Polymers

Oxygen modifies the response of high molecular weight hydrocarbons to irradiation, the main effect being oxidative degradation of the polymer molecules. The addition of oxygen to the free radicals produced by radiolysis occurs whether the C-C or C-H bond is broken. The addition of oxygen followed by chain cleavage can occur not only to free radicals but also

to double bonds formed by the splitting off of molecular hydrogen [57]. The diperoxides and hydroperoxides formed are relatively stable, but at high temperatures they decompose and can be used for the preparation of grafted polymers [58].

It is obvious that the rate of oxidation and peroxidation will depend on the dose-rate only if sufficient oxygen is present in the sample. Otherwise the rate-determining step will be the diffusion of oxygen, and the rate of oxidation will become independent of the dose rate. It is possible, in principle, under fixed conditions of sample geometry, permeability of the polymer and oxygen pressure, to determine the dose-rate compatible with the complete utilisation of the free-radicals formed in the polymer.

Dissolved oxygen can either enhance or decrease the degradation of polymers in solution, The degradation is again the result of reaction between polymer radicals and oxygen, sometimes giving immediate breakdown, and sometimes hydroperoxides and peroxides, which decompose slowly after irradiation [59,60].

In cases where oxygen suppresses degradation, the radicals formed by the reaction of polymer radicals with oxygen are probably degraded less readily than the polymer radicals themselves [61]. On the other hand,

acceleration probably occurs when this effect is over-balanced by the increased attack by peroxy radicals formed from the solvent [61,62].

C. Autoxidation

The term autoxidation normally refers to the slow spontaneous reaction of substances with molecular oxygen at moderate temperatures. The reaction usually takes place in the liquid state. In general terms, the process can be represented by the following reaction mechanism:

initiator	$\xrightarrow{ki}$	$2\ R^1$	(1)
$R^1 + O_2$	$\longrightarrow$	R^1O_2	(2)
$R^1O_2 + RH$	$\longrightarrow$	$R^1O_2H + R$	(3)
$R + O_2$	$\xrightarrow{fast}$	RO_2	(4)
$RO_2 + RH$	$\xrightarrow{kp}$	$RO_2H + R$	(5)
$2\ RO_2$	$\xrightarrow{kt}$	inactive products	(6)

A chain reaction may thus occur under the above conditions, the initial product usually retaining a single oxygen-oxygen bond. In the above mechanism, the first product is a hydroperoxide, which may be oxidised further or may decompose thermally to start new chains. When reaction (4) is assumed to be so much faster than (5), on account of the lower reactivity of RO_2 compared with R, the mechanism yields the rate equation (for long chains):

$$\text{rate} = \left(\frac{ki}{kt}\right)^{\frac{1}{2}} kp \left[\text{initiator}\right]^{\frac{1}{2}} \left[RH\right]$$

Termination can be assumed to occur entirely by reaction (6) when $\left[R\right] << \left[RO_2\right]$ [63].

The reactivity of a carbon-hydrogen bond to the atom transfer reaction (5) is greatly affected by the presence of a double bond or an aromatic ring, or by allyl substituents on the carbon atom. In each of the latter instances, the resulting free radical R is considerably stabilised. It must be pointed out, however, that addition of RO_2 to the double bond can also occur.

1. Aliphatic compounds

(a) Saturated hydrocarbons

It is apparent from the general mechanism already quoted that the reaction can be separated into three stages.

The initation involving homolysis of the hydrocarbon, R H,

$$RH \longrightarrow R + H \qquad (1)$$

can be produced by thermal decomposition of substances already present or deliberately added to the reaction mixture. Photoinitiation is also possible. The autoxidation reaction can become autocatalytic if initiated by a peroxide. In this case, the hydrogen atom is abstracted by radicals formed by the homolytic decomposition of the organic peroxide. Metal ion catalysis is often used

to increase the rate of initiation.

The propagation stage consists of the reactions:

$$R + O_2 \longrightarrow ROO. \qquad (2)$$

$$ROO. + RH \longrightarrow ROOH + R \qquad (3)$$

As stated previously, the reaction of alkyl radicals with oxygen is very fast, and the rate of oxygen consumption is found to obey the rate equation for long chains at oxygen pressures of ca.50mm. In the liquid phase, a dependence on oxygen is found at lower oxygen pressures. Due to the decreased oxygen content of the solution, reaction (2) can no longer be considered fast compared with (3).

In general, however, the cleavage of the RH bond by a peroxy radical is slower by a factor of 10^6 - 10^8, and this is the rate-determining step which governs the overall rate of autoxidation.

Termination depends principally on the relative importance of the reactions:

$$2R \longrightarrow R.R \qquad (4)$$

$$ROO. + R \longrightarrow ROOR \qquad (5)$$

$$2ROO. \longrightarrow ROOR + O_2 \qquad (6)$$

which, in turn, are dependent on the structure of the hydrocarbon, RH, and the concentration of oxygen. Under intermediate conditions of oxygen concentration and of stability of R, reaction (5) will predominate.

Molecules which donate a hydrogen atom to RO_2 to give stable products also inhibit the reaction.

Simple saturated hydrocarbons have been found to give hydroperoxides in reasonable yield on autoxidation. Experimental conditions usually involve shaking the hydrocarbon with air at a slightly elevated temperature, and either relying on peroxide formed to initiate chains, irradiating with ultraviolet light or adding a radical source. Good yields are generally obtained only at low conversions, since the resulting peroxides tend to decompose, especially in the presence of radicals. The order of radical attack on C-H bonds is donated as $3^o > 2^o > 1^o$ [64].

Methyl and ethyl hydroperoxides have been prepared by the mercury photo-sensitized oxidation of methane and ethane at 25°C, probably according to the following reaction scheme[65]:

$$Hg + h\nu \longrightarrow Hg^* \qquad (1)$$

$$Hg^* + RH \longrightarrow Hg + R + H \qquad (2)$$

$$R + O_2 \longrightarrow RO_2 \qquad (3)$$

$$RO_2 + RH \longrightarrow RO_2H + R \qquad (4)$$

Isobutane can be autoxidised to t-butyl hydroperoxides in the gas phase in the presence of hydrogen bromide at 158°C [66]. However, if secondary or primary alkyl hydroperoxides are formed from straight chain alkanes under similar conditions, decomposition occurs and ketones or

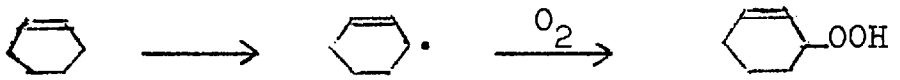
aldehydes and acids are isolated.

In cyclohexane the methylene groups are all equivalent and cyclohexylhydroperoxides can be prepared by autoxidation[67].

(b) Unsaturated hydrocarbons

It has long been known that simple olefins, after prolonged exposure to air, show typical peroxide reactions. Autoxidation was once believed to lead first to the formation of cyclic peroxide groups, and later to glycols or products of chain scission[68]. There was little direct evidence to support such a formulation beyond the fact that (i) the unsaturation of the autoxidised substance usually decreases progressively as oxygen-uptake increases, and (ii) the reaction frequently ends in hydroxylation of the double bond to yield a 1:2 - glycol, or in complete scission of the carbon chain at the double bond.

It is now well established that the reaction of simple olefins gives an allylic hydroperoxide through the formation of a radical at the α - carbon atom[69]:



Formation of such allylic hydroperoxides is typical of a wide variety of olefins, and the reactions show all of the qualitative characteristics of radical chain processes.

After reviewing the literature on the oxidation of

aliphatic compounds, Mayo[70] concluded that hydrocarbons of the structure $RR'C=CH_2$ give the most epoxide and least hydroperoxide or autoxidation. Allylic hydroperoxides are major oxidation products of most aliphatic mono-olefins of other structures, but epoxides and cleavage products also appear.

Twigg[71] has proposed a reasonable mechanism for epoxide formation in which peroxide radicals add to ethylenic bonds:

$$MO_2 + H_2C=CRR' \longrightarrow MO_2CH_2\dot{C}RR' \qquad (1)$$

Reaction (1) occurs instead of the removal of allylic hydrogen atoms:

$$MO_2 + RR'C=CR''CH_2R''' \longrightarrow MOOH + RR'C=CR''CHR''' \qquad (2)$$

The resulting radical from raction (1) then splits off an epoxide unit:

$$MO_2CH_2\dot{C}RR' \longrightarrow MO + H_2C\overset{O}{\diagup\!\diagdown} CRR' \qquad (3)$$

and the alkoxy radical, MO, continues the oxidation chain becoming an alcohol or part of an ether, or possibly splits off another epoxide unit.

The relative reactivities of polysubstituted ethylenes in copolymerisation has shown that the most addition (reaction 1), and the least transfer of allylic hydrogen atoms (reaction 2), is to be expected in the reaction of peroxy radicals with compounds of the type $RCMe=CH_2$. In autoxidation too, the greatest amount of epoxides and the least amount of peroxides are formed from such compounds.

It is possible that high pressures of oxygen will retard formation of peroxide (reaction 2) and thus permit further growth of the radical and more cleavage by depolymerisation:

$$MO(OCH_2CRR'O)_n \longrightarrow MO + nCH_2O + nRR'C{=}O \quad (4)$$

Depending on its length and structure, the alkoxy radical resulting from reaction (3), in addition to undergoing the hydrogen transfer and possible epoxide formation reaction mentioned by Twigg, may also split out formaldehyde, or some other carbonyl compound. Thus cleavage products should accompany epoxidation.

(c) Ethers and Alcohols

Ethers are another group of compounds which are readily autoxidised:

$$RCH_2OR' + O_2 \longrightarrow \underset{\displaystyle OOH}{\overset{\displaystyle |}{R\overset{\displaystyle |}{C}HOR'}} \quad (1)$$

The reaction shows the auto-acceleration and susceptibility to added radical sources and inhibitors which is characteristic of a radical chain autoxidation. However, the initial hydroperoxides formed from the lower ethers have structures which easily rearrange, or decompose to the polyalkylidene peroxides[72],

$$\underset{\displaystyle OOH}{\overset{\displaystyle |}{R\overset{\displaystyle |}{C}HOR'}} \longrightarrow \left[RCH\begin{matrix} O \\ \diagup \\ \diagdown \\ O \end{matrix} \right]_n \quad (2)$$

The initial product from the autoxidation of an

aliphatic alcohol is undoubtedly a hydroxyhydroperoxide, which then equilibrates with the corresponding ketone and hydrogen peroxide,

$$R_2CHOH + O_2 \longrightarrow R_2C(OH)(OOH) \rightleftharpoons R_2C{=}O + H_2O_2$$

It has been concluded that the reaction is a non-chain process because the radical $R_2C(OH)OO.$ cannot abstract hydrogen from the alcohol[73]. The products must therefore arise almost entirely from radical-radical termination reactions.

(d) Aldehydes

One of the most important and certainly the most studied type of autoxidation process is that undergone by aldehydes, in which the first stable product is a peroxy -acid. In many cases a radical chain process is well established[74], with initiation and propagation steps which can be generalised as:

$$RCHO \longrightarrow R\dot{C}O + H \qquad (1)$$

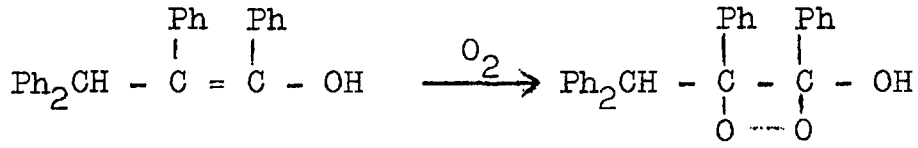
$$R\dot{C}O + O_2 \longrightarrow RCO.OO. \qquad (2)$$

$$RCO.OO. + RCHO \longrightarrow RC(OOH){=}O + R\dot{C}O \qquad (3)$$

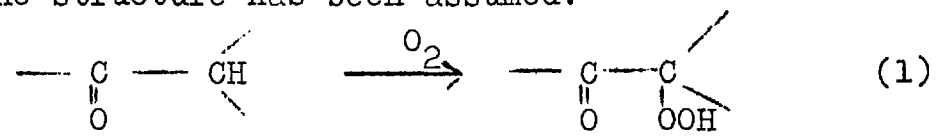
(e) Ketones and Enols

It has been shown that ketones, particularly thosewhich enolize readily, absorb oxygen to form peroxides. Early workers, however, partly on account of the erroneous picture of the autoxidation of olefins,

ascribed to these peroxides structures of the type:

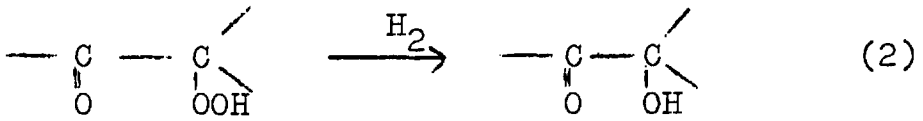


In all cases where further peroxides have since been prepared from similar ketones or enols, the hydroperoxy-ketone structure has been assumed:



(1)

In a number of cases, the structure of the hydroperoxide has been determined by reduction to the corresponding α- hydroxyketone:

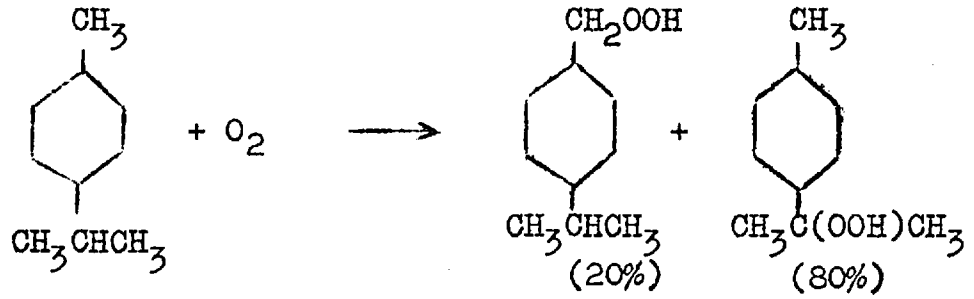


(2)

2. Aromatic Compounds

Many aromatic substituted hydrocarbons are readily converted to hydroperoxides, often in good yield under reaction conditions similar to thos employed with saturated aliphatic hydrocarbons. Nevertheless, autoxidation at a methyl group attached to an aromatic ring occurs only with difficulty. Simple methyl-benzenes appear to undergo autoxidation rather slowly so that hydroperoxide formation competes only weakly with decomposition. Thus no benzyl hydroperoxide has been isolated from toluene, although the hydroperoxide prepared by a different route

is reasonably stable in the absence of free radicals[75]. The ∝-methylene group of a longer side-chain in an aromatic ring is appreciably more reactive than the methyl group. Autoxidation is also found to occur most readily at an ∝-tertiary carbon atom. This latter fact and the lower reactivity of the simple methyl group are shown directly in p-cymene, where 80% of the radical attack occurs on the isopropyl group[76]:

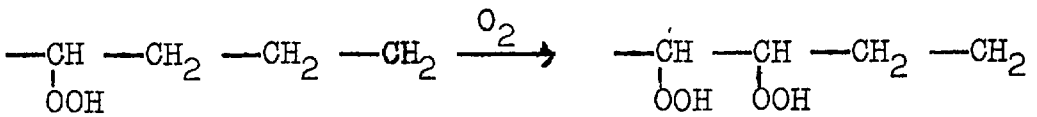


The best results are usually obtained at ca. 100°C, and yields are improved if the autoxidation is carried out on an aqueous emulsion in the presence of sodium carbonate or other weak bases, which stabilise the hydroperoxide against decomposition.

3. Polymers

Studies of the thermal oxidation of polythene have shown that the rate of oxidation becomes appreciable at 80°C; the rate increases with temperature, becoming rapid near the melting point. Notley [77] has followed the progress of oxidation in the temperature range 140-170°C. by volumetric uptake of oxygen. A formal

comparison was made with the kinetics of oxidation of a low molecular weight liquid hydrocarbon at a constant pressure of oxygen, and it was suggested that a mechanism of hydroperoxide formation would account for the initial stages of the reaction. However, in the oxidation of a liquid hydrocarbon, the hydroperoxide is a homogeneous catalyst. In contrast, it was proposed that hydroperoxide in the polymer hydrocarbon system influences only neighbouring units in the chain:



In subsequent reactions, the hydroperoxide decomposes to the secondary products which include carbon dioxide, water, aldehydes, ketones, acids and alcohols. The reaction therefore produces hydroperoxide, but not of a type which will catalyse oxidation of other molecules.

Little or no work on the autoxidation of polymers in solution appears to have been reported.

D. The Present Research

1. Previous work on the ethylene-oxygen system

During studies on the effects of ionizing radiation on hydrocarbons in aqueous solution, Henley and Schwartz[78] investigated the oxidation of ethylene. This oxidation was found to lead to the production of acetaldehyde with G values (G = molecules/100eV) as high as 60, when

solutions equilibrated with 1:1 ethylene-oxygen mixtures under a pressure of 8 atm. were irradiated with gamma-rays from cobalt-60 at a dose-rate of 2 x 10^5 rads/hr. Ethanol and acetic acid were also produced later in the reaction, but with much smaller G-values. Hydrogen peroxide was formed in solutions equilibrated with the gas mixture under atmospheric pressure at an initial rate corresponding to a G-value of 20. This value increased with increasing gas pressure, rising to an order of magnitude comparable with the aldehyde values at 8 atm.

Henley and co-workers[79] later observed G-values for aldehyde production as high as 200 from 1:1 ethylene-oxygen mixtures dissolved in water under pressures ranging from 12 to 50 atm., and irradiated with Co^{60} gamma-rays. An increase in the total pressure and dose was found to decrease these G-values; indeed the aldehyde appeared to act as inhibitor for its own formation, as it quickly attained a steady state concentration, which decreased with increasing pressure of ethylene and oxygen above 10 atm. Analysis showed in fact that about 25% of the aldehyde formed was formaldehyde; the remainder was assumed to be acetaldehyde. Alcohols, acids, hydrogen peroxide and organic peroxides were also products of the reaction; however, the yields of these compounds were much smaller.

The same system was studied by Weiss et al.[80], when the existence of a chain reaction at pressures below 10 atm. became open to some doubt. Co^{60} gamma-irradiation of water saturated with ethylene at 1 atm. in the absence of oxygen was found to give low yields of aldehydes, mainly acetaldehyde and n-butyraldehyde, and hydrogen peroxide, together with an oily polymer. From water saturated with different ethylene-oxygen mixtures, again at 1 atm., the principal irradiation products were acetaldehyde, glycolaldehyde and hydrogen-peroxide, all formed with G-values about 2. Formaldehyde and an organic hydroperoxide were formed in small yield. Irradiation of aqueous ethylene-oxygen solutions at higher pressures (up to 10 atm.) showed that the products and their yields did not differ markedly under these conditions from those obtained at lower pressures.

2. General aims of the current work

A study of the ethylene-oxygen system in aqueous solution is of particular interest in view of the high irradiation yields obtained from ethylene compared with saturated hydrocarbons. The reason why one set of workers obtained results consistent with a chain mechanism and the others did not is by no means clear, although it has been suggested that chain characteristics may appear quite suddenly as the relative concentrations

of oxygen and the organic reactant in the solution are varied[81].

The present work was initiated, therefore, to provide additional information on the radiation chemistry of the aqueous ethylene-oxygen system, with gas pressures above the solution in a similar range to those used earlier, i.e. 10 - 50 atm. The principal difference between this work and the earlier investigation over the same pressure range is the analysis of the primary products formed at relatively low total doses. Furthermore, particular attention has been paid to the application of very sensitive analytical methods for the detection and estimation of these products, since their nature and the variation of their concentrations with experimental conditions give valuable evidence regarding the reaction mechanism.

SECTION II

EXPERIMENTAL

CONTENTS

		Page
A.	Design and construction of apparatus	
1.	Introduction	56
2.	Pressure vessel	56
3.	Glass irradiation vessel	59
4.	Gas handling system	65
5.	Explosive hazard and precautionary measures	72
6.	Gas bubbling and liquid sampling system	77
B.	Materials	
1.	Gases	
(a)	Ethylene	85
(b)	Oxygen	86
2.	Other materials	
(a)	Water	87
(b)	Sulphuric acid	87
(c)	Ferrous and ferric ammonium sulphate	87
(d)	Hydrogen peroxide	87
(e)	β-Hydroxyethylhydroperoxide	88

Page

C. Procedure

1. Deaeration and preparation of solutions at high pressures 90

2. Irradiation of solutions under pressure 94

3. Post-irradiation handling of solutions 95

4. Dose-rate determination 96

5. Identification and determination of reaction products 100

(a) Aldehydes 102

(i) Formaldehyde 109

(ii) Acetaldehyde 113

(iii) Propionaldehyde 114

(iv) n-Butyraldehyde 114

(v) Glycolaldehyde and Glyoxal 115

(b) Peroxides

(i) Hydrogen peroxide 117

(ii) Hydrogen peroxide and organic hydroperoxides 118

(iii) Paper chromatography of peroxides 119

(c) Organic acids 121

(d) Alcohols 122

(e) Polymer 124

Page

6. Other analytical methods

(a) Determination of ferrous ions in the presence of ferric ions 127

(b) Determination of ferric ions in the presence of ferrous ions 128

D. Pulse radiolysis experiments

1. Introduction 128

2. Irradiation facility 129

3. Experiments with ethylene solutions

(a) In the absence of oxygen 130

(b) In the presence of oxygen 130

A. Design and construction of apparatus

1. Introduction

It was initially decided to investigate the radiation-induced oxidation of ethylene in aqueous solution at normal temperatures with gas pressures above the solution ranging from one to fifty atmospheres. Since glass cannot be used at elevated pressures, a metal system was assembled in which the pressurisation and subsequent irradiation of the solutions could be carried out.

If cyclinders containing the compressed gases at 100 to 200 atm. are used as a source of gas, then no further apparatus is necessary to obtain high pressures. The purity of the available gases (Section IIB) was found to justify their use directly from cylinders, so that purification and subsequent compression was not necessary.

The high pressure system consisted quite simply, therefore, of a steel irradiation 'bomb', which was pressurised directly from distribution vessels containing the individual reactant gases, and suitable means for evacuation of the vessels and pressure lines before admission of the pure gases to the system.

2. Pressure vessel

In accordance with the established design of high pressure vessels, a small capsule was constructed which

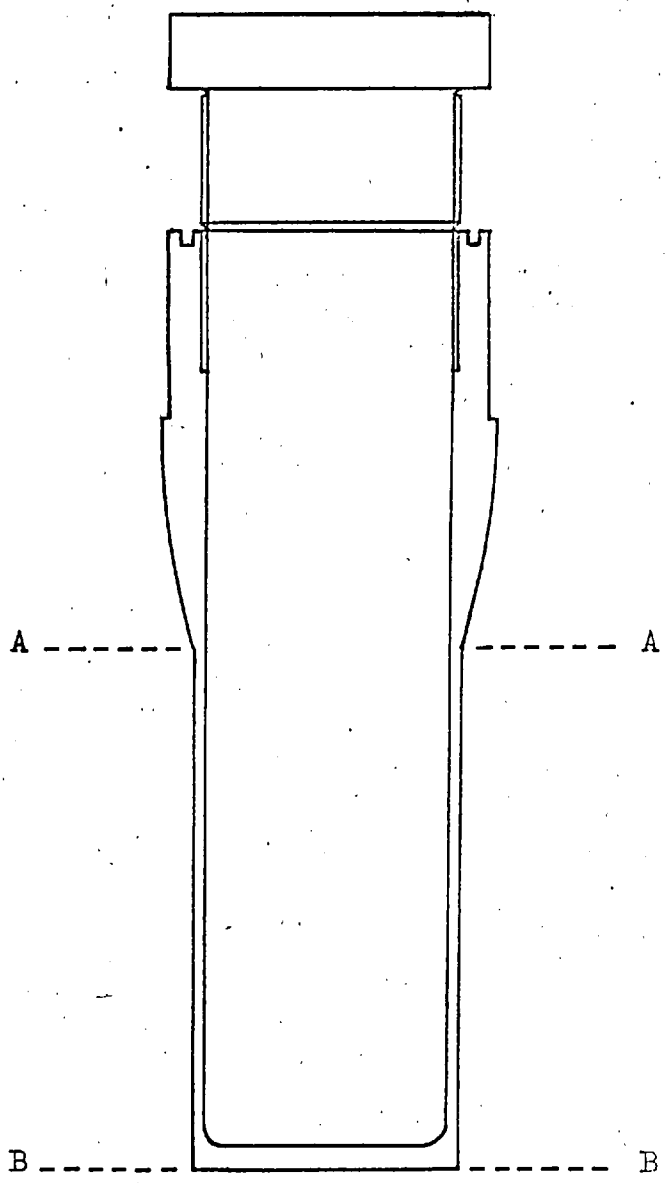
consisted of a hollow body with a heavy screw-in cap. The final design of the capsule is shown in Figure 1. After consideration of various alternative constructional possibilities as well as of the explosive hazard of the gas system, the body of the vessel was machined out of solid stainless steel rod (3½ in. diameter).

The high pressure seal between the cap carrying the gas inlet lines to the vessel and the main body of the vessel was achieved by the use of a standard rubber 'O' - ring lying in a machined groove at the sealing interface. The screw thread in the cap of the vessel (2¼ in. B.S. Whitworth) was appropriate to the pressure range over which it was proposed to carry out the irradiation experiments.

The gas-lines were coupled to the cap of the vessel through three parallel male stud couplings tightened down on copper gaskets. The internal diameter of the channels carrying these couplings was ⅛ in. The walls of the vessel between the diameters AA and BB were ⅛ in. thick to provide adequate safety without too much absorption of gamma-ray energy. By placing this section of the vessel in a position immediately adjacent to the source capsule, a reasonably homogeneous field of irradiation could be established. The shielding from this particular thickness of stainless steel amounts to something less than two per cent for 1.2 MeV Co^{60} gamma-rays[82]. When sealed, the

Figure 1.

Scale: 1/2



internal volume of the vessel was approximately 625 cm^3. (Plate 1).

It was obviously important to maintain the screw-thread between the cap and the body of the vessel in good condition by use of a graphite lubricant. If this was neglected, it is quite possible to cause damage to the thread while sealing off the vessel under spanner pressure. Flats were machined on th body of the vessel to allow it to be clamped securely in a simple vice. The insertion and removal of the glass irradiation tube was thus easily carried out.

3. Glass irradiation vessel

It was decided that the dissolution of the reactant gases in water under pressure should be carried out in a glass vessel contained inside the stainless-steel pressure vessel. This would avoid any effect attributable to the metal surface and provide a better control of the experimental conditions.

The form of the glass vessel is shown in Figure 2. The conical shape allowed the water to be frozen inside the vessel during de-aeration without the possibility of breakage. In the early stages of the work, it was visualised that dissolution of the gas mixture above the water might be effected by mechanical shaking of the whole pressure vessel assembly. A cap was therefore included

Plate 1.

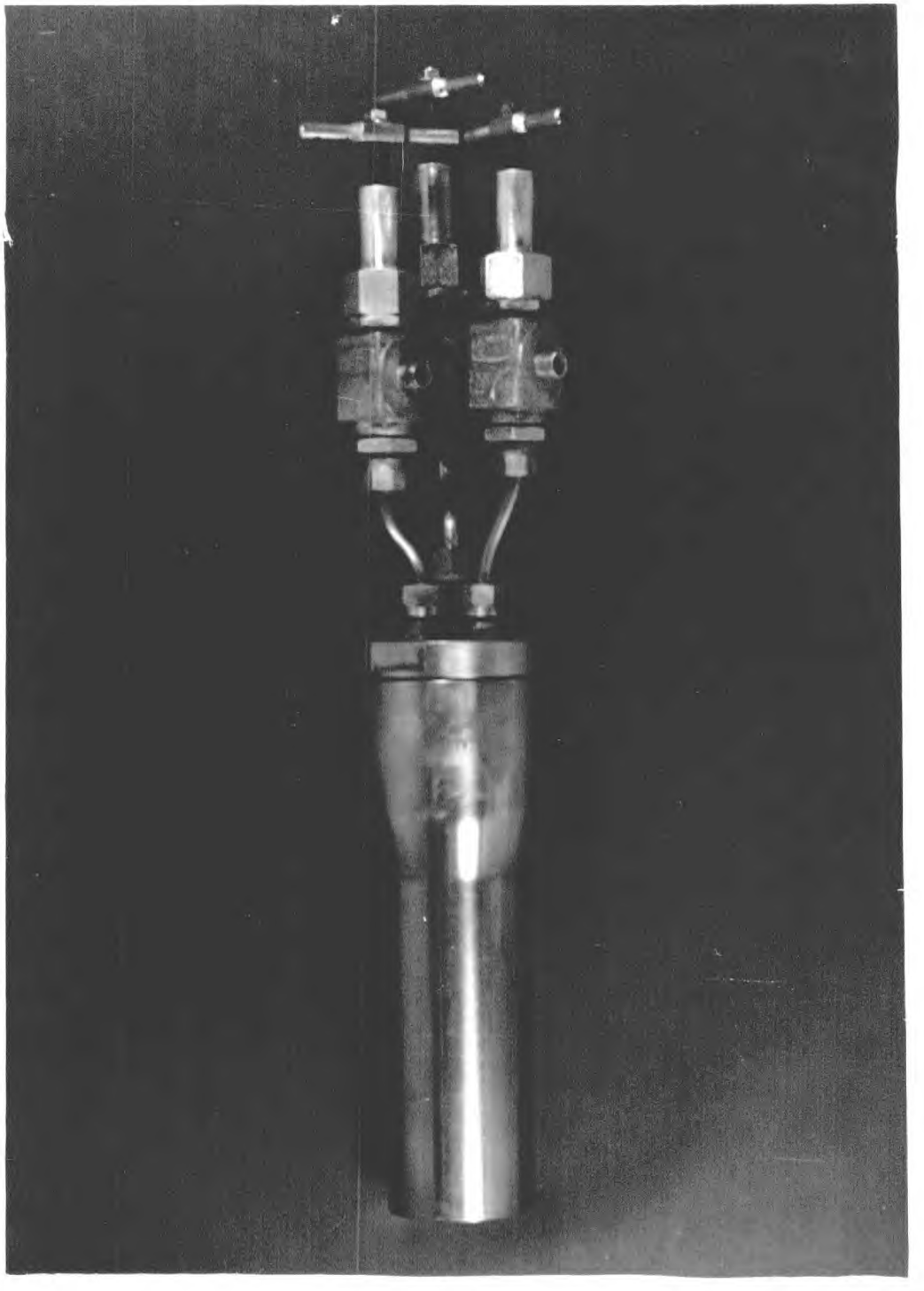
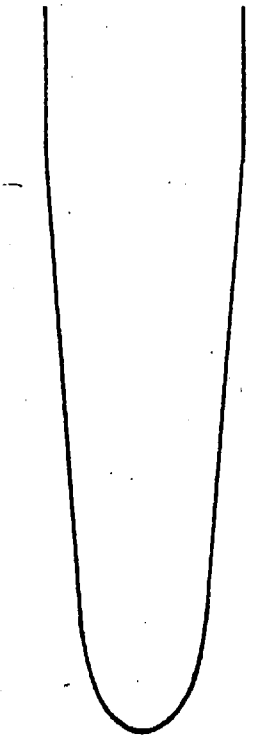


Figure 2.

Scale: 1/2



in the design of the glass vessel to prevent the solution being splashed into the body of the vessel. However, the impracticability of this procedure was soon realised, and with the dispersion of the gases through the solution by means of a bubbling tube, the necessity for a cap on the glass vessel was eliminated.

The critical shape of the glass vessel in relation to the various packings used to reduce the gas space inside the steel capsule has proved an important factor. The original packing between the walls of the two vessels consisted of Ballotini (Grade 12) glass beads, and proved to be very inconvenient in use.

Experiments involving deaeration of the system were carried out using this glass packing as a support for the irradiation vessel. In the ideal case, deaeration of liquids can be achieved by freezing to low temperature, evacuating the space above the frozen liquid, closing the tap to the pump and then allowing the frozen liquid to melt under vacuum. The liquid is then frozen again, pumped on, and the cycle repeated once or twice.

It was found, however, that, although the water inside the steel pressure vessel could be frozen within ca. 30 min., subsequent melting took place much more slowly. This was almost certainly due to the high insulation of the small glass beads and the polished steel surface surrounding

the vessel. Using controlled external electrical heating, the minimum time for the warming-up process was 1½ hr. In this process, care was taken to ensure that the final temperature of the water was not raised above the temperature at the start of the cycle, i.e., that prior to immersion of the pressure vessel in the liquid refrigerant, as this would result in substantial evaporation losses. The total time for a complete cycle, therefore, was about two hours, and at least two such cycles would be necessary to achieve satisfactory outgassing of the liquid.

However, in order to reduce the time involved in the outgassing cycle, ethylene gas was first passed through the triple-distilled water, and then one complete freezing cycle was carried out on the vessel. This practice was adhered to throughout the experimental work.

A magnetic follower, encased in polythene, was used inside the glass irradiation vessel, and the stirring was controlled by a rotating magnet placed below the base of the pressure vessel. The vessel was prevented from coming into contact with the magnet casing in order to minimise any heating effect which might result during prolonged stirring of the solution. The use of glass followers was found to be impracticable due to the abrasive action of the glass on the irradiation vessel.

The original glass vessels were found not to give

very efficient stirring of the solutions, so that a slight modification was made to the design. A new vessel was introduced with a much reduced taper to the sides and a flat bottom to accommodate the magnetic follower. The very fine glass beads inside the pressure vessel were, at the same time, replaced by larger glass balls (1.5 to 2 mm. diameter) which certainly facilitated manipulation of the inner glass vessel. Nevertheless, it soon became apparent that the failure rate for the revised design of the vessel was very much higher.

Asbestos wool was selected as a suitable alternative packing material for the vessel. The binding properties of this material allow it to be pressed tightly into position around the glass tube located centrally inside the steel capsule, thus forming a close-fitting mould from which the tube can be readily withdrawn. It was hoped that the increased resilience of the packing would result in a lower breakage rate for the glass vessels.

Some improvement was observed, but it eventually became necessary to revert to the original sharply-tapered vessels. Although this resulted in some slight reduction in the efficiency of the stirring action, the increased strength during the outgassing cycle was immediately apparent. These sharply-tapered vessels have since proved to be satisfactory in every respect.

4. Gas handling system

The form of the high pressure gas-handling system is shown diagrammatically in Figure 3. It is permissible to use standard copper pressure capillary tubing (¼ in. outside diameter, 16 s.w.g.) throughout the system, since at normal temperatures, reaction of ethylene with oxygen under pressure cannot be sensitised by the metal surface.

The high pressure pipe couplings fitted throughout the system were manufactured by the British Ermeto Corporation Ltd. The joint, which consists of a body portion, a nut and a sealing ring, resembles an ordinary compression joint. The sealing ring is not, however, compressed on to the surface of the pipe, but as the nut is progressively tightened, it moves along the pipe and cuts into it. In this way, the ring is made to throw up in front of it a ridge of displaced metal. It is this metal interlock that embodies the sealing principle of the joint. The depth of cut is controlled, and there is no fear of cutting so deeply that the pipe is weakened.

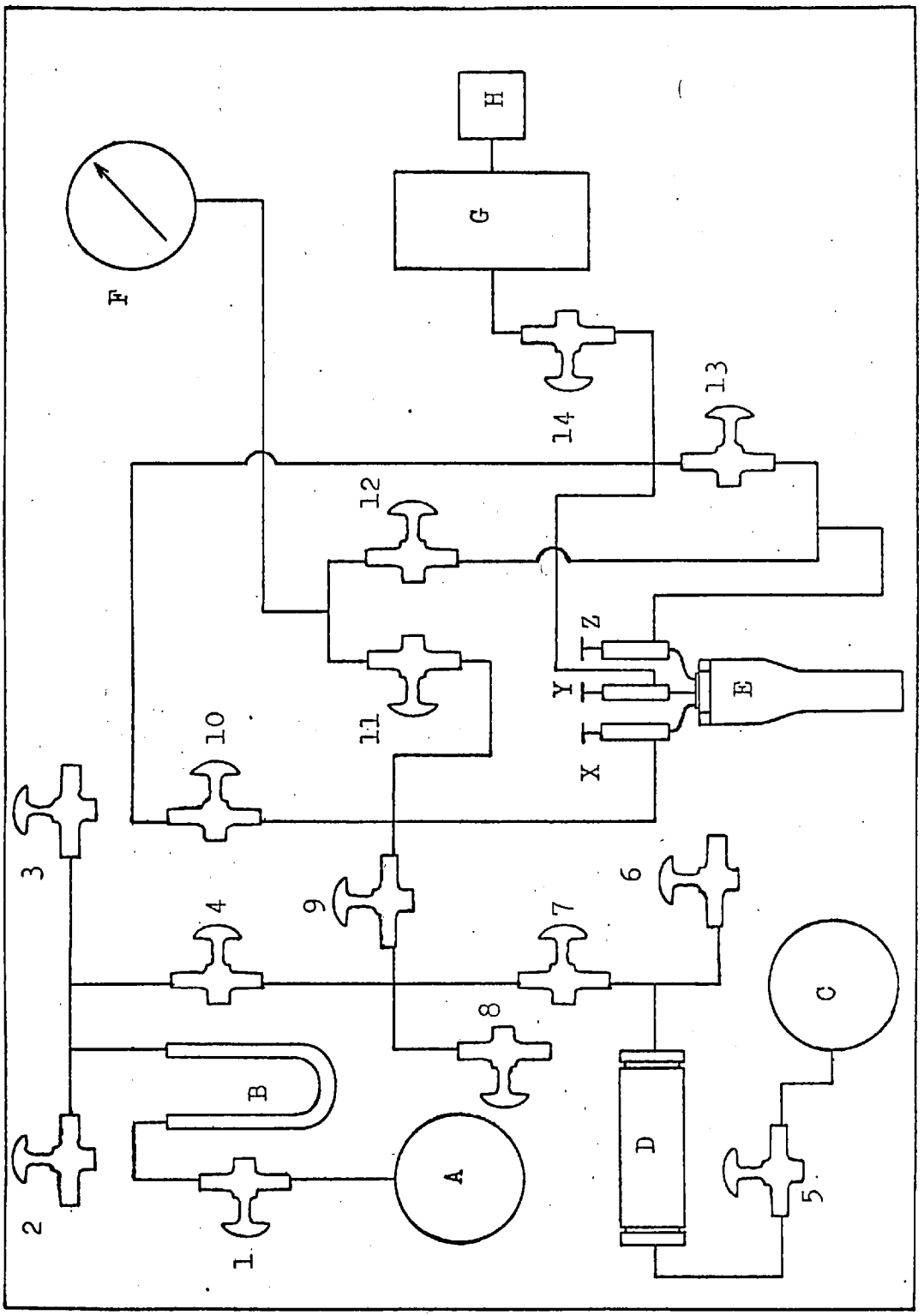
During the making of the joint, the ring is altered in shape, and its leading edge becomes embedded in the pipe. When the joint is broken, the ring remains permanently attached to the pipe-end. Thus the couplings can be broken and re-made almost indefinitely without affecting their efficiency. This was particularly advantageous

Figure 3.

KEY

A	Ethylene gas cylinder
B	Liquid trap / metering-vessel in ethylene gas-line
C	Oxygen gas cylinder
D	Steel metering-vessel in oxygen gas-line
E	Pressure vessel (containing solution under pressure)
F	Pressure gauge
G	High vacuum pumping-unit
H	Rotary oil-pump
X,Y and Z	Fine-control valves on pressure vessel
1 - 14	Shut-off valves in gas-lines

Figure 3.



when after pressurisation the steel capsule had to be removed from the high pressure system in order to carry out an irradiation.

In addition to acting as the sealing member, the ring also functions as a spring washer between the nut, the coupling body, and the surface of the pipe. For this reason, the couplings can remain completely pressure-tight even after prolonged periods of heavy vibration. Brass fittings together with nickel-plated brass sealing rings were used in conjunction with the copper piping.

When attempts were made to equilibrate the solutions with the gas mixture by mechanical shaking, it became necessary to couple the pressure vessel to the gas-handling system through flexible high pressure hose assemblies. In deference to the explosive hazard of the system, and to provide a more efficient means of dissolving the reactant gases under pressure, the flexible hose was replaced by standard metal piping.

The shut-off valves in the gas-feed lines, together with the three fine-control valves fitted to the pressure vessel, were built to specification and supplied by the British Ermeto Corporation Ltd. These valves were designed primarily for use in oil-hydraulic systems, but can operate with non-corrosive gases at normal temperatures without loss of efficiency.

Ermeto high pressure bonnet-type shut-off valves (standard series, type IV) were used in the gas lines. The specification states that these mild steel valves are suitable for use with compressed air and other non-corrosive gases at a maximum working pressure of 200 atm.

The valves fitted to the pressure vessel through short lengths of stainless-steel pressure capillary tubing were Ermeto fine-control valves (standard series, type III). These are designed for precise control of gases with a small rate of flow. The mild steel valves of this type also conform to the earlier specification. The standard rubber seals fitted as gland packings allow satisfactory use of the valves even after quite prolonged periods of irradiation. However, the regular replacement of the gland packings successfully contributed towards more efficient operation, and ensured that no loss of pressure occurred through leakage under irradiation conditions.

As mentioned previously, the compression of the gas cylinders was used to obtain the required pressure inside the steel irradiation vessel. Individual gas feed-lines eliminated the possibility of mixing in any part of the system other than inside the pressure vessl (Figure 3.) Valves venting to the atmosphere were situated at appropriate points to release the gas pressure before evacuation of the line.

The metering vessels in both gas-lines distributed small volumes of each gas under pressure to the steel vessel containing the solution. These vessels were filled by simple equilisation of pressure with the gas cylinders.

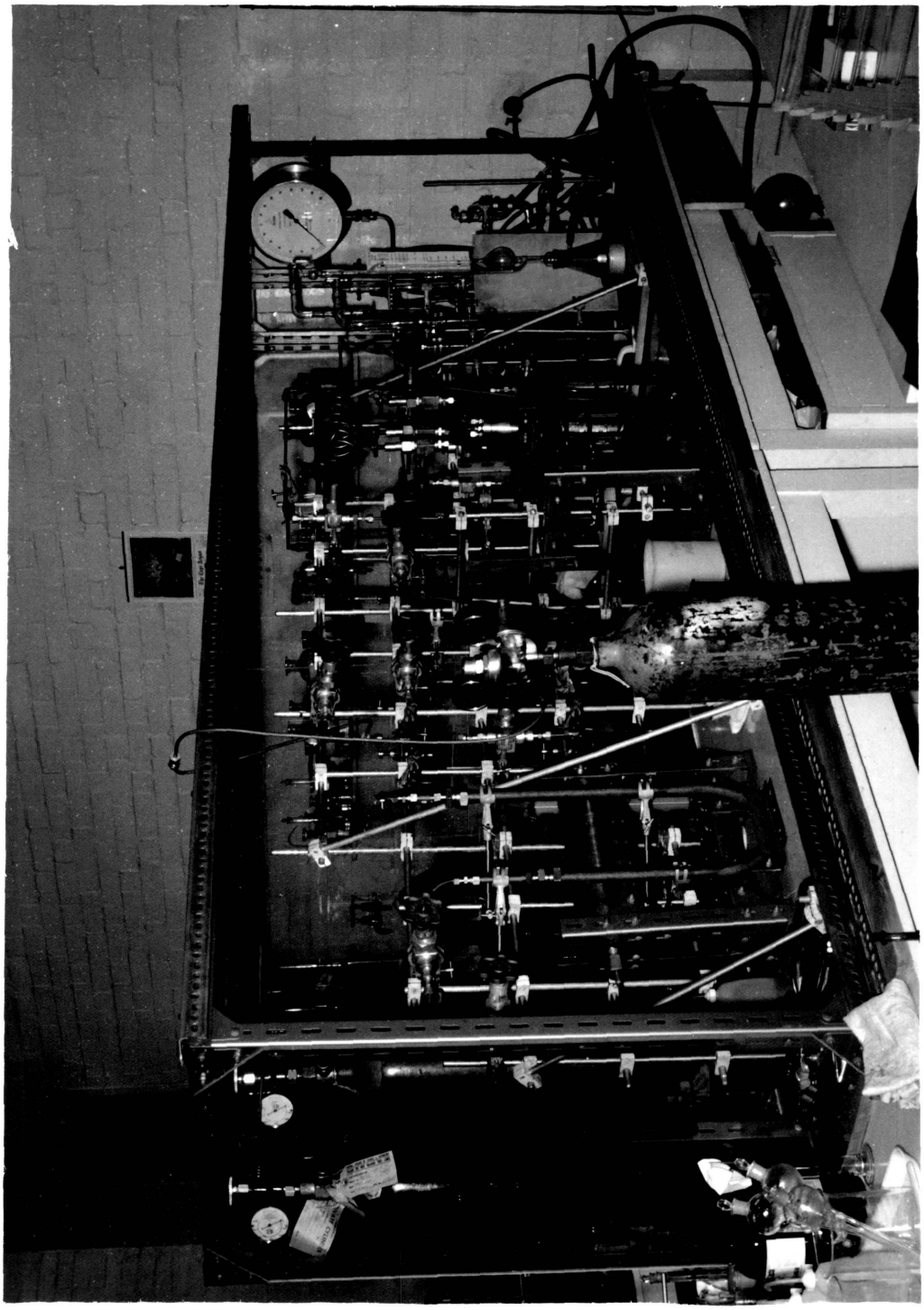
During pressurisation of the irradiation vessel, each of the reactant gases was admitted separately to the required partial pressure, and it was therefore necessary to be able to measure these pressures accurately. For this purpose, a Budenberg pressure gauge was employed, which was suitable for use with ethylene and oxygen over the pressure range 0 - 50 atm., and which had a guaranteed accuracy of $\pm$½%.

In the event of explosion, the gauge was fitted with a blow-out back. Care was taken during installation of the gauge to facilitate convenient operation and yet minimise hazard. The gauge was, therefore, mounted at the extreme end of the apparatus with the back six inches clear of a wall (Plate 2.)

The system was evacuated by a mercury diffusion pump, backed by a single-stage oil rotary pump, attached to the end of the high pressure line. Two liquid nitrogen traps were placed before the diffusion pump, and a tube packed with silica gel was interposed between the diffusion pump and the oil pump.

The whole high pressure system was supported in a

Plate 2.



vertical plane by conventional laboratory scaffold materials, with the shut-off valves clamped securely to the braced framework. The heavy metering vessel in the oxygen line was independently supported in a metal cradle and arranged horizontally in the system. The steel irradiation vessel was itself mounted in a steel framework, which provided adequate support, and at the same time, allowed the vessel to be manipulated without physical movement of the whole assembly.

5. Explosive hazard and precautionary measures

The explosive properties of ethylene even in the absence of oxygen have been clearly recognised for some time. For example, Waterman and his co-workers[83] have pointed out that ethylene under about 200 atm. pressure and at 350°C will decompose into its elements with explosive force. Even polymerisation at 60 atm. pressure, when promoted by a finely divided nickel catalyst, occurs vigorously at room temperature, and may give rise to an explosion[84].

The experience already quoted emphasises that the utmost care is needed when working with ethylene even at comparatively low pressures and temperatures. The possibility of explosion in the gas phase when working with mixtures of ethylene and oxygen at pressures up to 50 atm. was therefore given careful consideration.

The stoichiometry of an explosive reaction between

ethylene and oxygen is given by the equation:

$$C_2H_4 + 3\,O_2 \longrightarrow 2CO_2 + 2H_2O$$

This reaction is exothermic to the extent of 331.6 kcal. $mole^{-1}$.

It is a well recognised fact that a flammable mixture of gases, such as ethylene and oxygen, may be diluted with one of its constituents or with other gases until it is no longer flammable. The limit of flammability is the borderline composition at which a slight change in one or other direction produces either a flammable or non-flammable mixture. There are clearly under given physical conditions, two limits of flammability, i.e., a lower and a higher limit, only within which a flame can propagate itself[85,86]. These limits are usually defined in terms of the percentage of combustible gas present.

An increase in pressure does not always widen the limits. On the contrary, the range of flammability of some mixtures is narrowed by increased pressure, so that a mixture that can propagate flame at atmospheric pressure may not be able to do so at higher pressures. Since, however, measurements of limits are generally made in closed vessels, the results relate to pressures which increase at an unknown rate and to an unknown extent during the experiments. Thus in studies of the explosion under high pressures of ethylene mixed with oxygen, no

dangerous detonation was observed, but the maximum pressure attained at the instant of explosion was about ten times the initial pressure[87].

In general, the lower limit of flammability is nearly the same in oxygen as in air, but again, few strictly comparable results are available to show whether small differences exist. The effect of a reduced oxygen content of the 'atmosphere' with which a combustible gas is mixed has a marked effect in lowering the upper limit of flammability. However, when explosions occur in mixtures of fuel with air instead of oxygen, there is not much change in the explosion temperature, but the violence is reduced.

The limits of flammability of ethylene in oxygen, as determined by several sets of workers[88,89,90] are presented in Table 1.

Generally speaking, therefore, only mixtures of ethylene and oxygen lying outside the above limits of flammability were handled in those sections of the high pressure system unable to accommodate an explosion.

An explosion was most likely to occur when oxygen was admitted to the irradiation vessel against a pressure of ethylene. The prevention of possible flame propagation in the oxygen line was therefore of just importance.

The first steps taken to minimise the explosive hazard at this stage involved reduction of the free space inside

TABLE 1

Limits of flammability of ethylene in oxygen at normal temperatures and atmospheric pressure.

Limits, vol. % Ethylene		Ref.
Lower	Higher	
4.1	61.8	88
3.1	79.9	89
2.9	79.9	90

the vessel. This was achieved by packing with fine glass beads or asbestos wool, and in addition, by increasing the volume of solution from 100 to 150 ml.

Although the installation of a flame trap and bursting disc assembly between the gas cylinder and the pressure vessel would substantially reduce the risk of a flame striking back into the cylinder, this necessity was relieved by insertion in the oxygen line of a steel metering vessel of sufficient strength to accommodate the force of an explosion. This had a volume of ca. 500 $cm.^3$, and was coupled directly in the high pressure line by screwed brass adaptors. This vessel was evacuated and then filled with oxygen direct from the cylinder. In this way, it was possible to confine any explosion within the apparatus, and at the same time, attain the pressure of the gas mixture necessary for irradiation purposes.

During testing of the apparatus and preliminary experiments, the whole system was surrounded by ¼ in. perspex sheeting. The frontal working area of the apparatus was then accessible through four sliding perspex panels mounted in an overlapping arrangement. The high pressure couplings and valves were tested by admission of nitrogen to sections of the apparatus at a pressure of 10 atm., and then by observation of the corresponding rates of leakage in the defective parts of the system.

The gas leaks were found to be best detected by the application of concentrated soap solution around the couplings.

The protection provided by the perspex was adequate for these purposes, but virtually useless in the event of a really high pressure burst. Prior to the high pressure experiments with gas mixtures, therefore, the apparatus was moved into a corner of the laboratory, and two large (5 ft. x 4 ft. x 2½ in.) cocoanut-fibre gymnasium mats were secured in position along the working face of the apparatus. At the moment of admission of oxygen to the pressure vessel, it was only necessary to adjust the fine-control valves on the cap of the vessel. Sufficient access for this purpose was obtained between the mats. When not in use, the mats were sufficiently flexible to be folded back on top of the framework supporting the perspex panelling.

6. Gas bubbling and liquid sampling system

The first modification carried out on the pressure vessel in order to incorporate a glass bubbling tube in the cap was the enlargement of the existing channel connected to the fine-control valve X (Figure 3). This channel was increased to an outside diameter of 11/32 in., and sunk to a depth of ¾ in. into the screw cap. This allowed a ⅛ in. nominal bore glass capillary tube to be sealed into

position, and to match accurately the existing channel through the cap. The part of the capillary tube immersed in the solution was shaped into position along the central axis of the vessel, and then sealed into the cap of the vessel with a resin-bonded adhesive (Araldite). Thick-walled glass capillary tubing was used to provide increased strength over ordinary glass tubing during the freezing cycle, and also to facilitate the seating of a glass tube in the cap of the vessel.

The straightforward use of this tube for slow bubbling of the reactant gases through the solution is apparent, but the reverse process involving sampling of the irradiated liquid presented other problems. Before modification of the pressure vessel, the effect of sampling on the irradiation products was determined. Reduction of the pressure above a liquid sample will certainly cause any unreacted gases to come out of solution. In this case, the unreacted gas would largely consist of ethylene, but since the temperature of the liquid sampled would normally be close to the boiling point of acetaldehyde ($21^{o}C$), some decrease in the concentration of acetaldehyde might also be expected.

The approximate volume of gas which escaped from a liquid sample was calculated from the individual solubilities of the reactant gases in water. The

sampling conditions were simulated by bubbling the appropriate volume (200 $cm.^3$) of nitrogen through 25 ml. of a 5 x 10^{-4} M aqueous solution of acetaldehyde at different temperatures, and determining the decrease in acetaldehyde concentration. An approximately 20% loss of aldehyde was obtained in solutions treated at 23°C. However, there was no detectable loss when solutions cooled to 1°C were examined. The collection of samples from the pressure vessel was facilitated by cooling the tube leading out of the sampling valve, and by passing the irradiated liquid into a cold trap. 1 ml. samples of the solution were taken from the pressure vessel at regular intervals during irradiation, and that volume of the solution remaining in the sampling tube during a single irradiation period was discarded. This method overcame the obvious difficulty of dosimetry in such a system.

Some trial experiments were made with the simple glass capillary tube already described sealed in position inside the pressure vessel. This proved to be unsatisfactory due to the very high rate of pressurisation necessary to prevent the solution 'sucking-back' into the gas line. Indeed, at this stage of the experimental work it became necessary to place a vessel in the ethylene feed-line to prevent the possibility of water getting back into the gas cylinder. A liquid trap which consisted

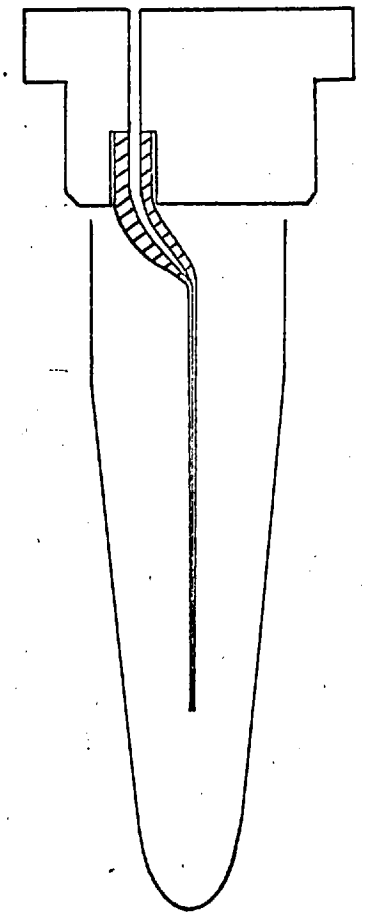
of a length of wide-bore copper pressure tubing that had been cold-worked into a large U-tube was therefore incorporated in the high pressure line (Figure 3). The internal volume of this trap was approximately 300 $cm.^3$, so that it served also as a metering vessel for distribution of the ethylene gas under pressure into the solution.

Due to the failure of the original bubbling/sampling tube, an alternative glass micro bubbling-tube was constructed by drawing out a short length of standard wide-bore capillary tubing. The simple arrangement of this tube when sealed into position in the cap of the pressure vessel is shown in Figure 4. When this arrangement was tested by slow passage of ethylene gas under pressure through the solution, no 'sucking-back' took place due to the reduction of the gas/liquid interface in the bubbling tube. This tube was found to be equally satisfactory in allowing controlled sampling of irradiated solution from the pressure vessel. For this purpose, a stainless-steel tube was fitted to the gas inlet-valve X, and cooled with an ice/water nixture in a surrounding sleeve during the sampling operation.

Experimental series of irradiations with ethylene in neutral solution (pH 5.5) under different gas pressures were successfully completed using this system. However,

Figure 4.

Scale: 1/2



it was found that the irradiation of dilute acid solutions (pH 1.2), using the sampling technique during irradiation, produced spurious results. Very high aldehyde yields were recorded at low doses. From the results thus obtained, it was found that the initial high aldehyde yield was quite reproducible, but fell away sharply with increasing dose. Further series of experiments at a pH of 1.2 were planned in order to examine the low dose region below 2×10^4 rads. However, a sample of the aqueous ethylene solution taken from the vessel prior to irradiation was found on analysis to contain an approximately 10^{-4}M concentration of acetaldehyde.

Experiments were then carried out at a number of points throughout the high pressure gas-handling system in order to trace and eliminate the source of the aldehyde. Ethylene gas trapped from the feed-line to the steel irradiation vessel was passed directly through a cooled sample of triple distilled water for several hours, and the resulting solution was analysed for acetaldehyde. There was no detecable concentration of aldehyde in the solutions prepared in this way. Solutions prepared similarly in dilute sulphuric acid (0.1N) were also found to contain no acetaldehyde.

A solution (pH 1.2) was then pressurised with ethylene gas, and the concentration of aldehyde in a number of liquid samples taken from the vessel under pressure was determined. This was then compared with the concentration of aldehyde in the unirradiated bulk solution. Three 10 ml. samples taken from the pressure vessel under 15 atm. of ethylene were found to contain a mean concentration of 8.5×10^{-5}M acetaldehyde. Analysis of the bulk solution showed that there was no aldehyde present.

It was apparent, therefore, that the factor common to the measured concentration of acetaldehyde in the solutions prior to irradiation was the use of a mild-steel sampling valve on the pressure vessel. This valve had been used successfully with neutral solutions, but the experiments carried out in dilute acid had caused some corrosion on the inner surfaces of the valve resulting in a large degree of contamination in the liquid samples passing through the valve under pressure.

A short investigation was made at this stage into the effect of a stainless-steel surface on a well-established radiation-chemical system. The ferrous sulphate system, which is widely used as a liquid dosimeter, was selected, since the oxidation yield of ferric ion can be readily determined by ultra-violet

absorption spectroscopy. A number of experiments made with stainless-steel vessels containing ferrous sulphate solution over a range of irradiation doses has shown that the measured concentration of ferric ion is equal to the concentration calculated according to a known dose-rate. It was concluded that the stainless-steel surface had no effect on the radiation chemistry of the system under these conditions.

A series of strictly comparable experiments in stainless-steel vessels was also carried out on an organic system, again in aqueous solution at a pH of 1.2. The acetaldehyde yield from the irradiation of 3×10^{-2}M ethanol solution was examined, and found to be completely independent of the surface of the irradiation vessel. Provided that the processes responsible for corrosion of a mild-steel surface were prevented, it was reasonable to suppose that contact between an irradiated solution and a stainless-steel surface can be tolerated. This latter condition can only be maintained if care is taken to ensure that the stainless-steel surface remains clean throughout a series of irradiation experiments.

In order to avoid any further discrepancy due to corrosion or other possible catalytic action inside the sampling valve, the mild steel valve X was replaced by a

valve of identical type and performance constructed in stainless-steel. This valve was tested to satisfaction, and was subsequently used successfully under a variety of experimental conditions.

B. Materials

1. Gases

(a) Ethylene

Ethylene, stated to be of 98.23% purity, was obtained at a pressure of 125 atm. from British Oxygen Gases Ltd. The removal of the many impurities from this gas at atmospheric pressure, and the subsequent necessity for an additional compression cycle, were given due consideration but later abandoned on account of the explosive nature of ethylene, even in the absence of oxygen, and of the large volumes of the gas involved in an operation of this kind.

In order to avoid the problem of recompression after purification, it was necessary to find a source of the pure gas at a practicable working pressure. A gas containing 99.8% ethylene and ca. 0.2% methane and ethane was available at approximately 15 atm. from I.C.I. (Heavy Organic Chemicals Division). It was possible to carry out some preliminary experiments in a pressure region below 10 atm., using a small cylinder of this gas.

However, the main supply of high purity ethylene gas

was obtained from Ethylene-Plastique. The purity quoted for this source was better than 99.97%, and the cylinder received had been charged with ethylene to a pressure of ca. 170 atm. The results of the analysis of this gas were as follows:

Inert	0.02%
Carbon dioxide	136 ppm.
Acetylene	8 ppm.
Oxygen	1 ppm.

The purity and high pressure of this supply made it suitable for the present experimental study. All the high pressure irradiations both in the presence and in the absence of oxygen were therefore carried out with this gas.

(b) Oxygen

Electrolytic oxygen was found to be available at high pressure (150 atm.) from British Oxygen Gases Ltd. A specimen analysis provided for a sample of this gas was as follows:

Oxygen	99.65%
Hydrogen	0.30%
Carbon dioxide	200 ppm.
Other C compds.	4 ppm.

Again the use of this gas directly from the cylinder can be justified on account of its high purity and compression. This gas, therefore, represented the oxygen

component of all the reactant gas mixtures irradiated in aqueous solution during the present study.

2. Other materials

(a) Water

From the point of view of radiation chemistry, it is often the traces of organic impurities present in the water which are the most troublesome, as these cannot be removed by ordinary distillation or by passage through ion-exchange resins. The principle employed to obtain pure water was the redistillation of good distilled water from alkaline potassium permanganate, followed by a single further distillation prior to collection. The pH of the triple-distilled water obtained in this way was always within the range 5.5 to 5.8.

(b) Sulphuric acid

For the irradiations carried out in acid solution, the pH of the triple-distilled water was adjusted to lower valvues by the addition of sulphuric acid. 'Analar' grade sulphuric acid, specific gravity 1.84, was used in the preparation of these solutions.

(c) Ferrous and ferric ammonium sulphate

'Analar' grade chemicals were again used.

(d) Hydrogen peroxide

The hydrogen peroxide solutions for irradiation were prepared by dilution of an inhibitor-free

10% w/w solution, which contained less than 1 ppm. NO_3^- and less than 0.5 ppm. Al^{3+}. The latter solution was supplied by Laporte Chemicals Ltd.

(e) β - Hydroxyethylhydroperoxide

In connection with a hypothesis introduced in a later Section, it was necessary to prepare a dilute aqueous solution of β-hydroxyethylhydroperoxide.

One well-established method of preparing the pure n-alkylhydroperoxides involves the reaction of n-alkyl methane sulphonates with 30% hydrogen peroxide[91]. In the present instance, this would involve reaction between the monomethane sulphonate of glycol and hydrogen peroxide:

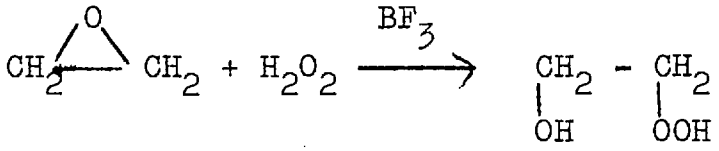
$$\begin{array}{l} CH_2O.\ SO_2.\ CH_3 \\ | \\ CH_2OH \end{array} + H_2O_2 \longrightarrow \begin{array}{l} CH_2OOH \\ | \\ CH_2OH \end{array} + CH_3SO_3H$$

The formation of a β-hydroxyhydroperoxide has in fact been reported after treatment of thymine with hydrogen peroxide in the presence of catalytic amounts of osmium tetraoxide[92].

However, Barusch and Payne[93] have suggested a route to the β-hydroxy alkylperoxides by the reaction of hydroperoxides with olefin oxides. Three of these peroxides have been prepared by reaction of t-butyl-hydroperoxide with the various epoxides, i.e., ethylene oxide, propylene oxide and isobutylene oxide; the yields obtained ranged from 33 - 43%. No attempt was made to develop optimum conditions to improve these yields, but it seems probable

that reactions of this type can be utilised as a general preparative method for β-hydroxy di-alkyl peroxides or hydroperoxides. The extension of this method to the synthesis of β-hydroxyethylhydroperoxide was therefore attempted.

This involved allowing ethylene oxide and hydrogen peroxide to react in the presence of a beron trifluoride catalyst:



The possible explosive nature of the reaction necessitated keeping the temperature of the reaction mixture at ca. 0°C; in addition the reaction was carried out in the presence of excess 30% hydrogen peroxide solution.

5 ml. of 30% hydrogen peroxide were cooled to - 10°C, and 0.5 ml. of ethylene oxide were distilled into the solution. A few drops of freshly distilled boron trifluoride-ether (boiling point 125 - 126°C) were then added, and the reaction mixture was set aside for 12 hr. at 0°C. Finally the mixture was warmed to room temperature, and the unchanged ethylene oxide (boiling point 10°C) was removed from the solution.

Mixtures of hydrogen peroxide and organic hydroperoxides can be quantitatively separated by complexing

the hydrogen peroxide with titanium (Ti^{4+}) ions, and precipitating the complex in alkaline solution[94]. In this way, a dilute aqueous solution of the hydroperoxide was obtained suitable for the measurements described in Section III.

C. Procedure

1. Deaeration and preparation of solutions at high pressures

The solubilities of ethylene and oxygen under normal conditions of temperature and pressure are given in Table 2. It is evident from these data that at ethylene pressures of 40 atm., the concentration in the solution equilibrated with the gas would be ca. 0.21M. During the present series of experiments, the maximum partial pressure of oxygen attained in a mixture of the reactant gases was approximately 14 atm. Under this pressure, the oxygen concentration in the solution corresponds to ca. 0.02M. Therefore, even in the solutions equilibrated with mixtures containing a high percentage of oxygen, the oxygen concentration would only approach one-tenth of the ethylene concentration.

Since ethylene is the more soluble of the two gases, it was necessary to equilibrate the solution first with respect to ethylene, and then with respect to the appropriate ethylene/oxygen mixture. In this way it was possible to reduce the loss of the less soluble gas from

TABLE 2.

Solubilities of Ethylene and Oxygen in Water

Measurements at 23°C, 760 mm. Hg.

Gas	Concentration	Ref.
Ethylene	5.21×10^{-3} M	95
Oxygen	1.41×10^{-3} M	96

the solution.

At the start of an experiment, 150 ml. of triple distilled water were sealed off inside the steel pressure vessel. The vessel was then coupled to the gas handling system through the fine-control valves X, Y, Z (Figure 3) on the cap of the vessel. The gas-line from the cylinder to the vessel was evacuated, and ethylene was passed slowly through the water inside the vessel by adjustment of the fine control valve X until a pressure of about two atmospheres was reached above the solution. Valve X was closed, and the solution inside the steel vessel was frozen by immersion of the body of the vessel in liquid nitrogen. All valves on the vessel were then fully opened, and the whole system was deaerated according to the method already described.

The metering vessel B and the gas-line between the cylinder and valve 4 were filled with a high pressure of ethylene (approx. 70 atm.), and the cylinder was isolated from the system by closing valve 1. With valves 7, 10 and 11 all closed, the high pressure gas stream was allowed to pass into the solution inside the pressure vessel by slightly opening valve X. Valves 13 and 14 were next closed under vacuum, and valve Z was slowly opened to admit the gas inside the vessel to the pressure gauge F. The gaseous ethylene in equilibrium with the solution was

then allowed to reach the required pressure, e.g., 20 atm., by observation of the gauge and adjustment of the valve X. When the necessary equilibrium had been attained, valve 4 was closed, and valve 8 was opened to the atmosphere to release the pressure in the gas-line.

After closing valve 8, the oxygen metering-vessel D and gas-line to the pressure vessel were evacuated with valves 7, 10 and 14 open. Valve 7 was closed, and the metering vessel was filled with oxygen from the storage cylinder to a pressure of ca. 100 atm. This volume of high pressure oxygen was isolated from the cylinder by closing valve 5, and the gas was distributed to the pressure vessel by opening valve 7, after first closing valves 10 and 14. Care was taken at this point to ensure that the oxygen pressure in the gas-line was greater than the ethylene pressure inside the vessel.

By careful control of the valve X, the oxygen was then admitted to the pressure vessel, again by bubbling the gas under high pressure through the solution. The pressurisation with oxygen was continued until the pressure of the gas mixture registered on the gauge corresponded to that required in the particular experiment. Valves X and Z were then tightly closed. In the oxygen line, valve 7 was closed and valve 8 was vented to the atmosphere. With valve 12 closed, the pressure inside the gauge was

very slowly released by opening valve 11. Valve 12 was then also slowly opened. The vessel containing the solution of the reactant gas mixture under pressure was finally uncoupled from the gas handling system, and irradiated separately inside the Co^{60} source-room.

2. Irradiation of solutions under pressure

Cobalt-60 is one of the most widely used artificial radioactive sources. It emits mono-energetic 1.17 and 1.33 MeV gamma-rays, and has a half-life of 5.3 yr. The associated beta radiation (0.31 MeV) is completely absorbed within the sealed capsule normally used to contain the isotope. A kilocurie Co^{60} source was used for the gamma-irradiation of all the solutions prepared under pressure inside the steel vessel. The metal isotope is contained inside a stainless-steel cylinder, 6 in. long and 0.56 in. in diameter, which eliminates the spread of activity. The source capsule is attached through a short length of stainless-steel rope to the end of a flexible cable. The drive for the source travel is provided by coupling the cable to an electric motor assembly. This enables the capsule to be moved by remote control through an S-shaped guide tube between the storage and the exposed position. The source room consists of a concrete catacomb-arrangement, which provides the necessary radiation shielding both while the apparatus is being set up prior to

irradiation, and during the operation of the source control[97].

During an irradiation, the pressure vessel was supported by a metal framework, and placed close to the source tube inside the chamber. A good reproducible irradiation position was thus attained. The dosimetry in this position is discussed in a later section.

Whenever samples of the irradiated solution were taken from the vessel under pressure by means of the sampling valve, it was found necessary to stir the solution inside the vessel before removing the sample. In practice, sampling of the irradiated solution was found to be reasonably efficient, and samples over the volume range 1 - 5 ml. were collected with the minimum of interruption consistent with continuity of the irradiation.

3. Post-irradiation handling of solutions

If the gas pressure above the solution was suddenly released after the vessel had been removed from the source-room, then the equilibrium between the radiolysis products and the unreacted gases would inevitably be disturbed. It has already been shown that this would result in serious losses of the more volatile aldehyde products from the solution, and it therefore became necessary to adopt the following technique when opening the vessel.

The solution after irradiation was quickly frozen in

a suitable liquid refrigerant, and the pressure inside the vessel equalised with that of the atmosphere. It was essential to thaw out the solution before attempting to unscrew the cap from the body of the vessel. At this stage it was again important to ensure that the final temperature of the solution did not rise above room temperature. This procedure minimises evaporation losses from the solution.

The vessel was clamped securely in a bench-vice to allow the cap to be removed smoothly and without loss of the irradiated solution. The glass irradiation vessel was then removed from its position inside the body of the steel vessel, and the solution was immediately analysed.

4. Dose-rate determination

For most radiation-chemical purposes it is more convenient to compare the amount of chemical reaction in the solution being studied with the amount of change in a standard system, the specific radiation yield of which has been determined by the use of primary physical standards. The use of the 'Fricke dosimeter', which consists of an air-saturated solution of ferrous sulphate in 0.8N sulphuric acid, is generally accepted as a convenient standard in chemical dosimetry of this kind[98]. In this system, the ferrous ion is oxidised to the ferric state, the oxidation of ferrous ions being coupled with the

reduction of oxygen in the solution. The use of the dosimeter is therefore limited by the concentration of oxygen present in the solution. Satisfactory results can be obtained in the dose-range 5,000 - 40,000 rads, but with inhomogeneous fields care must be taken that oxygen is not exhausted locally in the solution. The useful range in total dose can be extended about fivefold by saturating the solution with pure oxygen, although this was not necessary in the present investigation.

An approximately 10^{-3}M solution of ferrous ammonium sulphate was prepared in ca. 0.1N sulphuric acid. Water distilled from alkaline permanganate was used for the solution, since the one disadvantage of the 'Fricke dosimeter' is its sensitivity to organic impurities, which increase the radiation yield above the standard value. However, it was discovered that the presence of chloride ion (10^{-3}M sodium chloride) in the dosimetry solution could largely inhibit the chain reaction set up by organic impurities and ensure the correct yield value[99]. In acid solution, chloride ion is thought to react with hydroxyl radicals,

$$OH + Cl^- + H^+ \longrightarrow H_2O + Cl$$

and the resulting chlorine atom appears to oxidise ferrous ions more rapidly than it reacts with organic molecules.

The best method of analysis after irradiation of the

dosimetry solution is by spectrophotometric determination at 304 millimicrons of the ferric ions formed. At the wavelength concerned, the absorption of ferric ions in sulphuric acid has a maximum, while the absorption of ferrous ions is negligible. From a knowledge of the molar extinction coefficient, the corresponding concentration of ferric ions can be calculated.

The dosimetry experiments with the steel pressure vessel were carried out in the following way. The glass irradiation tube containing 150 ml. of the ferrous sulphate dosimetry solution was packed into position inside the steel vessel. The centre of the irradiation tube was made to coincide with the central axis of the steel vessel. The vessel was then clamped in the standard irradiation position near the cobalt-60 source, and the solution was irradiated to receive about 9,000 rads. The solution was stirred after irradiation in order to obtain uniform samples for the optical density determination made against a blank unirradiated solution in 1 cm. silica cells.

For cobalt-60 gamma-rays, the ferrous sulphate oxidation yield was taken to be $G(Fe^{3+}) = 15.5$[100], and the dose rate received in the solution was then calculated as follows.

Optical density (O.D.) = E x c x l

where E = molar extinction coefficient of ferric ion in 0.1N H_2SO_4 (litre.mole^{-1} cm.$^{-1}$).

C = concentration of ferric ions (mole.litre^{-1}).

l = optical path length in solution (cm.)

$$\therefore \quad c = \frac{O.D.}{E} \times 6.023 \times 10^{23} \text{ molecules. litre}^{-1}$$

and absorbed dose (eV/gm.) = $\frac{O.D.}{E} \times \frac{6.023}{15.5} \times 10^{23} \times \frac{100}{1000}$ in water

Since 1 rade = 6.24×10^{13} eV/gm.,

then dose (rads) = $\frac{O.D.}{E} \times \frac{6.023 \times 10^{22}}{15.5 \times 6.24 \times 10^{13}}$

The value taken for the ferric ion molar extinction coefficient in 0.1N sulphuric acid at 20°C. is 2115 litre. mole^{-1} cm.$^{-1}$ 100. This particular quantity has been found to increase unusually rapidly with temperature, i.e., to the extent of 0.7% per degree centigrade, so that the temperature of the solution during the optical measurement must be known.

$$\therefore \quad O.D._{20^\circ C} = O.D._{T^\circ C} \ (1 - 0.007t)$$

where t = T - 20

T = temp. of sample (°C.).

Substitution into the dose equation of the above value for E, and of the expression for the variation of optical density with temperature gives:

$$\underline{\text{dose (rads)}} = \frac{\text{O.D.}_T(1 - 0.007t)}{2115} \times \frac{6.023 \times 10^{22}}{15.5 \times 6.24 \times 10^{13}}$$

$$= \underline{2.94 \times 10^4 \ (1 - 0.007t) \ \text{O.D.}_T{}^{\circ}\text{C}}$$

From a knowledge of the irradiation time, the dose-rate in the solution can then easily be determined.

5. Identification and determination of reaction products

The problems of analysing very dilute aqueous solutions of organic compounds cannot readily be solved. In the present study, most of the individual product concentrations were of the order of 10^{-7} to 10^{-8} moles/ml., so that it was necessary to use mainly colorimetric methods of analysis.

Some consideration, however, was given to the various possible physical methods of identification. From the fact that aldehyde products in particular can be readily analysed by paper chromatography, it is reasonable to suppose that a suitable system of gas-liquid chromatography might be a convenient analytical tool. Although a sample containing a high percentage of water can be analysed by direct introduction of the sample on to a column, this method is not likely to find application for concentrations much below ca. 10^{-3}M. The alternative method, which involves removal of the volatile products from the solution, has been used fairly widely but is nevertheless likely to

be subject to considerable errors.

Direct measurement of the absorption spectra of the irradiated solutions presents a further possible method of examination of the reaction products. However, the radiolysis products obtained from the present system would not be expected to show strong ultra-violet absorption in dilute solution, so that determination of individual compounds from the spectra would be extremely difficult. Infra-red spectroscopic analysis of mixtures containing more than two components would again not be sufficiently quantitative to justify this means of examination.

Polaragraphy was given consideration particularly in connection with the estimation of peroxide products. Hydrogen peroxide and the lower alkyl hydroperoxides have previously been investigated polarographically in aqueous solution[101,102,103]. Quantitative analysis of mixtures at low concentrations (ca. 10^{-5}M) presents considerable difficulty, however, due to interference by hydrogen peroxide.

In the present study, therefore, it was necessary to resort almost entirely to colorimetric analysis for each class of compound present in the irradiated solutions. This method of analysis is highly sensitive and very specific. Most of the available methods can readily be applied both to single substances and to mixtures, and in many cases there is no interference due to the presence of other

compounds in the solution.

Methods of analysis had to be devised for the quantitative determination of (a) aldehydes, (b) peroxides, (c) acids, (d) alcohols, (e) polymer.

(a) Aldehydes

Paper chromatography of the 2:4-dinitrophenylhydrazones formed from the aldehydes present in the irradiated solutions was used as the means of identification. The procedure applied to the detection of simple primary mono-aldehydes was that described by Gasparic and Vecera[104].

5 ml. of 0.25% 2:4-dinitrophenylhydrazine in 30% perchloric acid were added to 20 ml. portions of the irradiated solutions, and the hydrazones formed were then extracted into carbon tetrachloride (25 ml.). The resulting extracts were concentrated under vacuum before application to the paper. Whatman No.4 paper was impregnated with a 25% solution of dimethylformamide in ethanol, and the ethanol was allowed to vaporise for 10-15 min. in air before the hydrazone derivatives were placed on the paper. Descending chromatography was then carried out with cyclohexane as the moving phase. The spots were visible on the paper, and a good separation was obtained from chromatograms run for a period of about four hours. Trace products were best identified on the paper after development of the colour by spraying with ethanolic sodium hydroxide

solution.

The R_F values obtained for the hydrazones of the pure aliphatic aldehydes were found to be in excellent agreement with the values given in Table 3. After development with ethanolic sodium hydroxide solution, the compounds enumerated could be detected on the paper by their red-brown colour.

It was possible to establish the relative amounts of the various aldehyde products from the chromatograms by elution of the undeveloped hydrazones separately from the paper. The individual spots were eluted into 5 ml. of ethanol, and the absorption of the solutions was compared at 360 millimicrons in a Unicam SP500 spectrophotometer. The product ratios were then calculated from a knowledge of the molar extinction coefficients of the hydrazones in ethanolic solution, using the values given in Table 4 [105,106]. From this representative series of compounds, it can be seen that there is little variation in the value of the molar extinction coefficient, E_{max}. The agreement between two sets of elution data obtained from similar chromatograms was found to be better than $\pm$ 2%.

An additional chromatographic system was also employed in order to provide evidence for the formation of aldehyde products other than the primary aliphatic

TABLE 3

R_F values of the aliphatic aldehyde 2:4 - dinitrophenylhydrazones [104].

Dimethylformamide-cyclohexane system

Compound	R_F
Formaldehyde	0.20
Acetaldehyde	0.32
Propionaldehyde	0.50
n - Butyraldehyde	0.66
iso - Butyraldehyde	
n - Valeraldehyde	0.76
iso - Valeraldehyde	
n - Hexylaldehyde	0.82
Dodecylaldehyde	0.91

TABLE 4

Absorption maxima and molar extinction coefficients of aldehyde - 2:4-dinitrophenyl hydrazones [105, 106].

Measurements made in pure ethanol.

Compound	λ max (millimicrons)	E max ($l.mole^{-1}cm^{-1}$)
Formaldehyde	344	18,200
Acetaldehyde	354	21,000
Propionaldehyde	356	21,800
n-Butyraldehyde	358	21,000

aldehydes already described. In particular, it was important to be able to detect the di-aldehyde, glyoxal, or the compound which forms the identical hydrazone derivative, glycolaldehyde. Chromatography of the concentrated solution of 2:4-dinitrophenyl-hydrazones prepared from the irradiated solution was therefore carried out on Whatman No.1 paper according to the method of Schmitt, et al.[107], using ascending phase chromatography and the solvent system dibutyl ether - dimethylformamide - tetrahydrofuran (85 : 15 : 4 in volume ratios). It was found that the primary aliphatic aldehydes moved together on the solvent front, whereas the 2:4 - dinitrophenylhydrazone derivatives of glycolaldehyde and glyoxal respectively gave identical R_F values. The latter compounds were easily identified as dark blue spots on spraying the paper with ethanolic sodium hydroxide solution.

The total aldehyde content of the irradiated solutions was determined quantitatively by the method of Johnson and Scholes[108]; this again depends on the formation of the 2:4 - dinitrophenylhydrazones in aqueous solution followed by quantitative extraction into carbon tetrachloride. The direct addition of ethanolic sodium hydroxide solution to the carbon tetrachloride extract produces a deep red-brown colour, which can be determined very sensitively by direct reading of the optical absorption at 430 millimicrons.

It is fortunate that the 2:4 - dinitrophenylhydrazones of most primary aliphatic aldehydes show a characteristic absorption at this wavelength. Using the ratios obtained by paper chromatography for the various aldehyde products present, together with the values of the molar extinction coefficients of the corresponding hydrazone derivatives in 0.1N ethanolic sodium hydroxide solution, the individual aldehyde concentrations in the irradiated solution could be calculated.

The following experimental procedure was adopted for the analysis of the irradiated solutions. 2-5 ml. of the hydrazine reagent were added to a 10 ml. portion of the irradiated solution. During sampling, the small sample of the irradiated solution (1 ml.) was diluted to 10 ml., and the analysis was carried out on this dilute solution. After addition of the reagent, the solution was set aside for 30 min. at room temperature to allow the formation of hydrazones to go to completion. The solution was then extracted by shaking vigorously for 1 min. with a 10 ml. aliquot of carbon tetrachloride. The aqueous layer was extracted a second time by shaking for 15 sec. with 2.5 ml. of carbon tetrachloride. 1 ml. of ethanolic sodium hydroxide solution was added to the combined carbon tetrachloride extracts in a 25 ml. volumetric flask, and the volume was immediately made up to the mark with ethanol.

The optical density of the solution was then measured within a few minutes of addition of the alkali. When formaldehyde was present in the irradiated solutions, it became important to note the exact time at which the measurement was made after preparing the solution. This enabled the appropriate correction to be made from the decay curve of formaldehyde 2:4 - dinitrophenylhydrazone. This correction is discussed more fully later in this section. With acetaldehyde, and other primary aliphatic aldehydes, it was sufficient to measure the optical density of the solution within 10 min. of preparation. In every analysis, a blank was performed concurrently with the actual determination. The value of the blank has been attributed to the extraction of hydrazine reagent by the carbon tetrachloride. Its magnitude depends on the pH of the aqueous phase and the time of shaking with the solvent. A standard procedure for the analysis was therefore essential in order to maintain a good degree of reproducibility between measurements.

Glyoxal 2:4 - dinitrophenylhydrazone, like other dialdehyde hydrazones, gives a purple-blue colour in strongly alkaline solution which enables measurements to be made at the absorption maximum, i.e., at 570 millimicrons. This colour was found to be stable for at least two hours.

In the application of this method of total aldehyde determination, individual calibration graphs of optical

density against concentration were obtained for the following aldehydes: (i) formaldehyde, (ii) acetaldehyde, (iii) propionaldehyde, (iv) n-butyraldehyde, (v) n-valeraldehyde, and (vi) glyoxal/glycolaldehyde. The standards for the calibrations were the crystalline derivatives prepared from the pure aldehydes. These were obtained by reacting ca. 0.1 gm. of the aldehyde with 3 - 5 ml. of a stock solution of 2:4 - dinitrophenylhydrazine sulphate in methanol. Precipitation of the product was then found to take place fairly slowly on cooling the solution. Each hydrazone was recrystallised from the appropriate solvent until the melting point was constant (Table 5).

Standard solutions of the hydrazones were prepared in carbon tetrachloride, and treated for calibration purposes in the manner already described for the irradiated solutions. Beer's Law was found to be obeyed at concentrations up to 10^{-4}M. The extinction coefficients found are listed in Table 6.

Several other analytical methods for aldehydes were employed in the examination of the irradiated solutions. These will now be discussed, together with outstanding points relating to the total aldehyde determination, under headings for the individual aldehydes.

(i) Formaldehyde

The decay characteristics of formaldehyde

TABLE 5

Characterisation of the aldehyde 2:4 - dinitrophenylhydrazones

Compound	Solvent of Crystallisation	M.P. °C (found)	M.P. °C (109,110)
Formaldehyde	Ethanol	166	167
Acetaldehyde	"	165	168(148)
Propionaldehyde	"	153	156
n-Butyraldehyde	"	123	123
n-Valeraldehyde	"	105	107
Glycolaldehyde	Nitrobenzene	) 320-325)	328
Glyoxal	"		

TABLE 6

Molar extinction coefficients of aldehyde 2:4 - dinitrophenylhydrazones measured in CCl_4 (0.1N alc.NaOH) at 430 millimicrons

Compound	E max. ($l.mole^{-1}$ $cm.^{-1}$)
Formaldehyde	8,250
Acetaldehyde	3,820
Propionaldehyde	3,000
n-Butyraldehyde	3,170
n-Valeraldehyde	3,430
Glycolaldehyde	13,280
Glyoxal	13,280

2:4 - dinitrophenylhydrazone in carbon tetrachloride have been mentioned previously. Decay curves have been measured using a recording spectrophotometer in order to establish the conditions for formaldehyde determination in the concentration range 10^{-5} to 10^{-6} M [111]. The maximum absorption at 430 milimicrons decreased by approximately 10% in 2½ min. after the addition of the alkali. All total aldehyde measurements (including formaldehyde) were therefore carried out at a standard time of 2½ min. after colour development in the solutions, and corrected for decay using the curves. This determination was found to be at least ten times as sensitive as the chromotropic acid method[112], although the latter was used for the specific estimation of formaldehyde in solutions that had been irradiated to high doses.

The fact that chromotropic acid (1,8 - dihydroxy-naphthalene - 3,6 - disulphonic acid) reacts with formaldehyde to form a violet solution, the optical density of which is a function of the formaldehyde concentration, has been made the basis of a colorimetric method of analysis. The method is claimed to be insensitive to acetaldehyde if carried out in strong acid solution, but in solutions containing a high ratio of hydrogen peroxide to formaldehyde quite strong interference has been noted[113]. Under these conditions, the hydrogen peroxide is best removed from the

solution by reduction with magnesium in 4N hydrochloric acid[114]; the formaldehyde concentration is not affected by this procedure.

The determination was carried out as follows. 50 mg. of the sodium salt of chromotropic acid were weighed into a 50 ml. volumetric flask containing 5 ml. of concentrated sulphuric acid. 1 ml. of the irradiated solution (from which hydrogen peroxide had been removed) was added, and the mixture was then heated for one hour on a steam bath, after which it was cooled and diluted to the correct volume with distilled water. The colour developed was measured at 580 millimicrons, and found to be stable for several hours. A calibration curve was obtained by dilution of a standard formaldehyde solution, which had been previously analysed by the sodium sulphite method. The molar extinction coefficient for the complex was found to be 14,670 litre. $mole^{-1}$ $cm.^{-1}$.

(ii) Acetaldehyde

The method of Johnson and Scholes[108] was found to be completely satisfactory. The hydrazone has a maximum absorption at 430 millimicrons so that the total aldehyde determination at this wavelength, together with the results of the paper chromatography, enabled the irradiation yield of acetaldehyde to be calculated. In alcoholic sodium hydroxide solution, the hydrazone

was stable for periods up to 10 min.

(iii) Propionaldehyde

Propionaldehyde reacts with ninhydrin (indane-trione) in concentrated sulphuric acid to produce a deep red-blue colour suitable for spectrophotometric analysis at a wavelength of 595 millimicrons[115]. However, formaldehyde inhibits the colour formation without itself reacting to give a complex, and consequently must be removed from the solutions. The formaldehyde was effectively separated from the propionaldehyde by conbination with aminoacetic acid. For the analysis of a sample of the irradiated solution in the absence of formaldehyde, the procedure adopted was as follows.

The ninhydrin reagent consisted of a 3% solution of indane-trione in 5% aqueous sodium bisulphite solution. 4 ml. of concentrated sulphuric acid were mixed with a 0.5 ml. aliquot of the irradiated solution in a volumetric flask. 0.2 ml. of the ninhydrin reagent were added; the solution was diluted to 5 ml. with 5% bisulphite solution, and then allowed to stand for one hour for the full colour intensity to develop.

(iv) n-Butyraldehyde

n-Butyraldehyde interferes with the determination of propionaldehyde if it is present in larger quantities than the propionaldehyde[115].

Equal or smaller amounts of n-butyraldehyde in relation to propionaldehyde may be determined quite successfully using the same method. The intensity of colour observed with n-butyraldehyde and the ninhydrin reagent is much less than in the previous case; the wavelength for maximum absorption is 470 millimicrons.

(v) Glycolaldehyde and Glyoxal

Glycolaldehyde and glyoxal both react with 2:4 - dinitrophenylhydrazone to form the same dialdehyde hydrazone. In strongly alkaline solution, the corresponding derivatives from each compound show identical spectra with maximum absorption at 570 millimicrons, the colour being stable for up to 2 hr. However, since this dinitrophenylhydrazone is relatively insoluble in carbon tetrachloride, benzene has been used to extract it from the aqueous solution.

The irradiated solution was treated with the 2:4 - dinitrophenylhydrazine reagent and extracted with benzene. The formation of a blue colour on addition of ethanolic sodium hydroxide solution to the extract would thus indicate the presence of either glycolaldehyde or glyoxal in the irradiated solution.

It is possible to differentiate between these two compounds using the method of Dechary, et al.[116]. This depends on the formation of a dark blue derivative when

glyoxal is heated with 2:3 - diaminophenazine in strong acid solution. The colour reaction is suitable for spectrophotometric analysis only after the required excess of 2:3 - diaminophenazine has been converted into phenazine by treatment with nitrous acid; the tetrazonium salt thus formed is subsequently reduced with hypophosphorous acid.

1 ml. samples of the irradiated solution were treated with 1 ml. of the colour reagent, which was prepared in 8.5 N acetic acid, and then heated together with the reagent blank in a boiling water bath for 10 min. After temperature equilibration in an ice/water bath, 1 ml. of 0.02% potassium nitrite solution and 0.5 ml. of 50% hypophosphorous acid were added, and the flask was again heated for 20 min. in the boiling water bath. After cooling, the solutions were made up to 5 ml. with distilled water, and the absorption was then measured at 570 millimicrons.

Glycolaldehyde, however, only reacts with the colour reagent under conditions when conversion into glyoxal can occur, i.e., in concentrated sulphuric acid. The reagent was therefore prepared by dissolving 21 mg. of 2:3 - diaminophenazine in 100 ml. of 10 N sulphuric acid.

1 ml. samples of the irradiated solution were pipetted into 5 ml. volumetric flasks together with 0.7 ml. aliquots of the colour reagent. 0.5 ml. of concentrated sulphuric acid were then also added to each of the flasks

before they were immersed in a boiling water bath for 1 hr. The reagent blank was identical with the test solution except that 1 ml. of 10 N sulphuric acid was used. The flasks were chilled in an ice/water bath before the addition of 1 ml. of potassium nitrite solution and 1 ml. of hypophosphorous acid. Finally, the solutions were heated in the water bath for a further hour, before dilution to volume and measurement of the fully developed colour, which was found to be stable even after 24 hr.

(b) Peroxides

(i) Hydrogen peroxide

Hydrogen peroxide was identified and determined by the titanium sulphate reagent[117].

The test reagent was prepared by dilution of 2.5 ml. of 15% w/v titanic sulphate solution to 250 ml. with approximately 0.1N sulphuric acid. 10 ml. aliquots of the irradiated solutions were treated with 10 ml. of the reagent and diluted to 25 ml. in a standard flask; the absorption of the yellow colour which developed immediately was then measured at 410 millimicrons. The low molar extinction coefficient of the titanium-hydrogen peroxide complex necessitated the use of cells of 4 cm. path length for the optical density measurements. This excluded the possibility of the determination being carried out on small samples of the irradiated solution

taken from the vessel under pressure.

A standard hydrogen peroxide solution was made by dilution of 20 ml. of 30% hydrogen peroxide solution to 1 litre with distilled water, and standardised by titration with potassium permanganate. The standard solution was further diluted to about 10^{-4}M for purposes of calibration, when the extinction coefficient of the titanic complex with hydrogen peroxide was found to be 273 litre.mole^{-1}cm.$^{-1}$ at 410 millimicrons.

The method, which is not sensitive much below concentrations of 10^{-4}M, can be applied specifically to the detection of hydrogen peroxide in the presence of hydroperoxides in both neutral and acidic solution.

(ii) Hydrogen peroxide and organic hydroperoxides.

The basis of the method of analysis for the total hydroperoxide in the irradiated solutions was the oxidation of iodide ion in neutral or slightly acid solution, followed by the measurement of the I_3^- ion at 350 millimicrons[118].

The reagent was prepared from two solutions containing: (1) 1 gm. of sodium hydroxide, 33 gm. of potassium iodide, and 0.1 gm. of ammonium molybdate in 500 ml. of water, (2) 10 gm. of potassium hydrogen phthalate in 500 ml. water. Equal volumes of the two solutions were mixed

shortly before use. At the pH of the mixed reagent, peroxide reacts rapidly with iodide in the presence of the molybdate catalyst.

Samples of the irradiated solution ranging in volume from 0.2 to 1 ml. depending on the peroxide concentration were mixed with 2.5 ml. of the reagent and diluted to volume in a 5 ml. volumetric flask. Optical density measurements of the tri-iodide ion formed in the reaction were carried out in 1 cm. cells at 350 millimicrons against the reagent blank.

The extinction coefficient of the I_3^- ion was determined using a series of peroxide solutions prepared by dilution of a standard hydrogen peroxide solution, and found to be 25,400 litre.mole^{-1} cm.$^{-1}$ at the wavelength for maximum absorption.

The method is very sensitive down to concentrations of 10^{-5} M, and both hydrogen peroxide and organic hydroperoxides may be estimated together when present in the irradiated solutions. The yield of organic hydroperoxide was then determined by subtraction of the hydrogen peroxide yield previously estimated by the titanium sulphate method.

(iii) Paper chromatography of peroxides

Paper chromatography is recognised as the most useful method for the qualitative analysis of

peroxide mixtures. The identification of specific peroxides in a mixture is only possible however if the pure peroxides are readily available for calibration purposes. Nevertheless the technique has been developed to allow at least the general classification of the individual peroxides after separation on paper.

Cartlidge and Tipper[119] have developed a paper chromatographic technique for distinguishing peroxides in a mixture. This technique is essentially a modification of two previously published methods[120,121]. In order to distinguish between hydrogen peroxide and hydroxy-alkyl-peroxides, the sample was placed on untreated Whatman No.3 paper clamped between two glass plates to prevent the evaporation of volatile components. A moving phase of 10 volumes of n-butanol, 10 volumes of ether, and 1 volume of water was then used for the development of the paper in descending chromatography. In this system, hydrogen peroxide has an R_F value of 0.50, and hydroxy-alkylperoxides 0.95-0.98. Alkylhydroperoxides and dialkylperoxides, together with peroxy-acids, move together at the solvent front (R_F = 1.00), the former spreading across it.

The presence of free hydrogen peroxide can be established by spraying the paper with ferrous thiocyanate, under which condition the limit of detection can be as low as 20μg. The chromatogram was sprayed first with a

dilute solution of o-tolidine and ferrous ammonium sulphate in aqueous acetic acid, and, again after any spots had faded, with ferrous thiocynate. Hydrogen peroxide, hydroperoxides and peroxy-acids give blue spots immediately with this spray but with dihydroperoxides and hydroxyalkylperoxides the colour develops more slowly. These latter spots can be made more intense by application of a 4% solution of hydriodic acid in glacial acetic acid.

(c) Organic Acids

A paper chromatographic method has also been described, for the separation and analysis of the volatile fatty acids[122]. For calibration purposes, the acids were dissolved in dilute aqueous ammonia, and the resulting solutions of their ammonium salts were applied to the chromatograms. The chromatography was carried out on Whatman No.4 paper, using a developing solvent which contained 70% propanol and 30% concentrated ammonia. The development time was generally ca.18 hr.

At the low concentrations of acids encountered in the experiments, it was very difficult to locate the spots on the paper when sprayed with a slightly alkaline solution (pH 9.5) of B.D.H. Universal Indicator. Another indicator consisting of 8-hydroxy-quinoline and zinc sulphate in water was found to be more satisfactory[123]. When sprayed with this indicator, the spots were detected

by their fluorescence under ultra-violet light. This system showed a reasonable separation between simple straight-chain aliphatic acids after chromatographic separation of the ammonium salts.

The sodium salts of possible acids formed during radiolysis were concentrated by evaporation of the irradiated solution, and then converted to the ammonium salts before separation was attempted. The method was therefore sufficiently sensitive to detect very small quantities of organic acids among the irradiation products.

(d) Alcohols.

A spot test for alcohols depends upon the formation of a vanadium (V^{5+}) complex with oxine in an acetate medium, the ratio of vanadium to oxine being 1:2. The complex is insoluble in water, but dissolves in benzene giving a dark greyish-green colour to the organic phase. If alcohol is added to the suspension of the vanadium complex in water and an extraction with benzene is carried out, the organic layer appears red[124]. It is presumed that in fact a second complex is formed with the alcohol which is more stable than the initial vanadium-oxine complex. A spectrophotometric method for the determination of simple primary alcohols has been based on this qualitative test[125].

1 ml. of ammonium vanadate solution (containing 1 mg.

of vanadium per ml.) and 1 ml. of a 2.5% solution of 8-hydroxy-quinoline in 6% acetic acid were added to 2 ml. of irradiated solution. 3 ml. of an acetate buffer (pH 4) were then added, and the mixture was continuously shaken for 20 min. with 15 ml. of benzene. After separation of the phases, extraction from the aqueous phase was repeated twice with fresh quantities of benzene and the other reagents.

When the aqueous phase contained insufficient alcohol together with the precipitate of vanadium oxinate, both the reddish colour of the alcoholic vanadium-oxinate, and the grey-black colour of the excess vanadium-oxinate were observed on extraction into the benzene layer. The benzene extracts were then washed collectively with 10 ml. of N sodium hydroxide solution so that the vanadium-oxinate was transferred to the aqueous phase, while the alcohol complex remained in the organic phase along with part of the excess oxine. If an alcohol was detected, the optical density of the combined extract was measured at 390 millimicrons against a reagent blank.

The absorption spectrum of the alcohol complex in benzene solution was usually determined for the first benzene extract from the alcohol solution. The highest absorption at a given concentration was observed with amyl alcohol, whereas absorption decreased from butyl to

methyl alcohol. In all spectra of the alcoholic vanadium-oxinate complex, two plateaux have been found in the regions, 370-400 millimicrons and 450-480 millimicrons. The first flat area of the spectrum is an area of maximum absorption for the complex. Determinations were therefore made at a wavelength of 390 millimicrons where the sensitivity of the method is highest, and the influence of oxine is very small.

(e) Polymer

Estimation of the polymer formed in the absence of oxygen was possible in many cases. This was usually achieved quite simply by removing the bulk water from a 20 ml. portion of the irradiated solution by careful evaporation on a water bath. This operation was usually carried out inside a glass weighing-bottle, and the polymer residue was finally dried to constant weight by evaporation over concentrated sulphuric acid inside a vacuum desiccator. Each weight determination of the polymer was carried out several times in every case. The agreement between determinations was often better than 2%.

When high pressure solutions of ethylene were irradiated to high doses (5×10^5 rads), it was found possible to filter the large polymer particles from a volume of the solution on to a sintered glass disc (porosity 5 microns). The glass crucible containing the

filter disc was then dried at 100° C. in an electric oven until a constant weight was registered for the separated polymer. The results agreed very well with those obtained by evaporation of smaller portions of the same solution, using the techniques already described.

The use of infra-red spectroscopy for the detection of end-groups on polymer chains has been discussed by Collinson and Dainton[126]. In a study of the radiation-induced polymerisation of acrylonitrile in aqueous solution, the best chance of detecting absorption by end-groups was considered to be under conditions where the lowest molecular weight product was obtained, i.e. the highest possible dose-rate and the lowest possible monomer concentration was used. Infra-red spectra of the polymer samples then showed absorption by hydroxyl groups in the region 2400-2100 $cm.^{-1}$ Extremely careful drying of the polymer samples had no apparent effect on absorption due to hydroxyl groups. Neither did the polymer prepared from pure monomer show any hydroxyl group absorption after standing in air for several days. This latter fact clearly indicates that the infra-red absorption observed for the polymer obtained in the irradiated solution is not due to absorbed water.

Infra-red spectra were therefore measured for polymer samples obtained under a variety of experimental conditions,

both with respect to the pressure of the dissolved gas, and the irradiation dose absorbed in the solution. The spectra were obtained using a Hilger H800 double beam infra-red spectrophotometer.

The most suitable method of sample preparation in this instance is the dispersion of the polymer in one of a number of possible media in the form of a mull. Nujol (high boiling fractions from petroleum) is the most commonly used mulling agent, together with hexachloro-butadiene, which is employed when it is desirable to study frequency ranges in which Nujol absorption bands appear.

The polymer sample (2 - 5 mg.) was well ground together with the appropriate mulling agent (1 drop) in a small agate pestle and mortar. The mull was transferred to a rock-salt plate by means of a micro-spatula, and then covered with a second plate which forces the mull to spread as a thin film between the plates. The plates were retained together in a metal holder to form the complete cell, and placed in the sample beam. Since all alkali halide plates give a constant background absorption, two similar plates were inserted in the reference beam of the instrument. In order to prevent an interference pattern, the plates forming the blank cell were maintained at a distance slightly greater than 1 mm. apart.

The plates are attacked by moisture, and it was

therefore assential to store them in a desiccator after use in order to avoid weak, broad, hydroxyl background absorption in the regions of 3,700 cm.$^{-1}$ and 1,600 cm.$^{-1}$.

6. Other analytical methods

(a) Determination of ferrous ions in the presence of ferric ions

The formation of ferrous ion in ethylene solutions irradiated in the presence of ferric ammonium sulphate was determined by complex formation with o-phenanthroline. The orange-coloured complex with maximum absorption at 510 millimicrons is a reversible oxidation-reduction indicator, which has been used for colorimetric estimation[127]. In a solution buffered to a pH of 4, the colour becomes stable within 15 min., and does not change for at least 48 hr.

1 ml. portions of the irradiated solution were pipetted into 10 ml. volumetric flasks, and diluted to 7 ml. with distilled water. 1 ml. of the buffer solution (pH 4) was then added to each sample, followed by 1 ml. of 0.25% o-phenanthroline solution. The solutions were diluted to volume, mixed well and allowed to stand for 30 min. The optical absorption at 510 millimicrons was then compared with a blank determination prepared from the unirradiated solution.

The calibration curve for the o-phenanthroline complex

was obtained by dilution of a standard solution of ferrous ion (ca. 5×10^{-4}M), and by treatment of the diluted solutions with the reagent. The molar extinction coefficient of the complex was calculated to be 12,840 litre $mole^{-1}$ $cm.^{-1}$.

(b) Determination of ferric ions in the presence of ferrous ions

At a pH of 1.2, the formation of ferric ion in ethylene-oxygen solutions irradiated in the presence of ferrous ammonium sulphate was measured directly by optical absorption of the solutions at 304 millimicrons. From a knowledge of the molar extinction coefficient of ferric ions, the yield of ferric ions can be readily determined.

D. Pulse radiolysis experiments

1. Introduction

A study of the kineties of radiation-induced chemical reactions has been made possible by the development of techniques similar to those used in flash photolysis. A single pulse from a linear accelerator, which can produce high energy electron pulses a few microseconds long, will deliver a dose of the order of several thousand rads to a few millilitres of liquid; in many cases this can result in a chemical change large enough to be easily detectable by optical absorption with a time resolution as low as 0.1 microsec. The identification of radicals produced

in this kind of experiment has already been briefly mentioned[22,53].

2. Irradiation facility

Irradiations were carried out at the Linear Accelerator Facility in the Scientific Apparatus Department, Associated Electrical Industries, Ltd., Manchester; the machine available produces 2 microsec. pulses of 4 MeV electrons. The irradiation cell consists of a thin-walled 'Pyrex' tube 20 mm. diameter and 50 mm. long, closed with quartz end-windows. The electron beam enters through the side of this tube, and a beam of light from a high-pressure mercury lamp passes along its axis. The optical system is arranged to focus the transmitted light on to the entrance slit of a monochromator and then on to a photocell. The photocell output passes through an amplifier, and is then applied to the vertical deflection plates of a cathode-ray oscilloscope, the horizontal sweep of which is arranged to start a few microsec. before the electron pulse. In this way traces are obtained showing the variation with time of the absorption at a selected wavelength of the liquid in the irradiation cell.

The effects of Cerenkov light and electrical interference have been minimised in this apparatus[128]. Both effects become negligible a few tenths of a microsecond after the pulse, and from this time onwards it is possible

to detect changes in light intensity of about 0.1 per cent.

3. Experiments with ethylene solutions

(a) In the absence of oxygen

A de-aerated solution of ethylene in water (pH 5.5) was produced by continuous bubbling of the gas for 10 hr. through the irradiation apparatus immediately before exposure.

The solution was introduced into the irradiation cell under gravity feed by means of a magnetically operated valve. In this way, a single pulse can be delivered to the sample, or alternatively higher doses can be obtained by continued pulsing on the same sample.

The reaction of solvated electrons with ethylene in the solution was examined at a wavelength of 510 millimicrons; in this instance, the dose per pulse delivered to the solution was ca. 100 rads. The absorption spectrum of the solution was also examined over the range 500 - 250 millimicrons under identical irradiation conditions.

(b) In the presence of oxygen

The solution (pH 5.5) was prepared by equilibration with a 1:1 ethylene-oxygen gas mixture. The dose per pulse was increased to ca. 5000 rads, and the absorption of the solution was measured over the range 510 - 230 millimicrons.

SECTION III

RESULTS

CONTENTS

Page

A. Aqueous solutions of ethylene in the absence of oxygen

1. Introduction 135

2. Effect of ethylene pressure

(a) Formation of polymer 135

(b) Formation of aldehydes 137

(c) Formation of hydrogen peroxide 140

3. Effect of dose

(a) Formation of polymer 140

(b) Formation of aldehydes 143

(c) Formation of hydrogen peroxide 143

(d) Other products 143

4. Effect of medium

(a) pH of the solution

(i) Formation of polymer 147

(ii) Formation of aldehydes 147

(iii) Formation of hydrogen peroxide 149

(b) Addition of other species

(i) Irradiations in the presence of ferric ions 149

(ii) Irradiations in the presence of hydrogen peroxide 151

Page

B. Aqueous solutions in the presence of oxygen

1. Introduction 153

2. Effect of total pressure of a given gas mixture 157

3. Effect of dose

(a) Formation of aldehydes 157

(b) Formation of peroxide products 163

(c) Other products 163

4. Effect of variation of oxygen concentration at a constant ethylene concentration in the solution 164

(a) Formation of aldehydes 164

(b) Formation of peroxidic products 169

(c) Identification of the organic hydroperoxide formed in the irradiated solutions 174

5. Effect of medium

(a) Irradiations in the presence of ferrous ions 179

(b) Irradiations in the presence of hydrogen peroxide 182

Page

C. Pulse radiolysis experiments

1. Introduction 182

2. Ethylene solutions in the absence of oxygen 186

3. Ethylene solutions in the presence of oxygen 188

A. Aqueous solutions of ethylene in the absence of oxygen

1. Introduction

Series of irradiations have been carried out on solutions of pure ethylene in various media over a range of gas pressures and doses; a dose-rate of approximately 9×10^4 rads/hr. was used throughout. Polymerisation of the ethylene is the main process under these conditions, although aldehydes and hydrogen peroxide are also formed.

2. Effect of ethylene pressure

(a) Formation of polymer

The formation of radiolysis products in the ethylene solutions was studied under gas pressures from 5 to 40 atm. The polymer yield at a total dose of ca. 5×10^5 rads is shown as a function of ethylene pressure in Figure 5.

At pressures below 10 atm., the reaction was accompanied only by a general cloudiness in the irradiated solution, and the appearance of an oily polymer on the surface. As the pressure of ethylene was increased above 10 atm., solid particles of polymer separated from the solution during radiolysis. These increased in size with ethylene pressure, at at high pressures coagulated quickly and floated to the surface of the solution. During the course of irradiation, the flotation of the

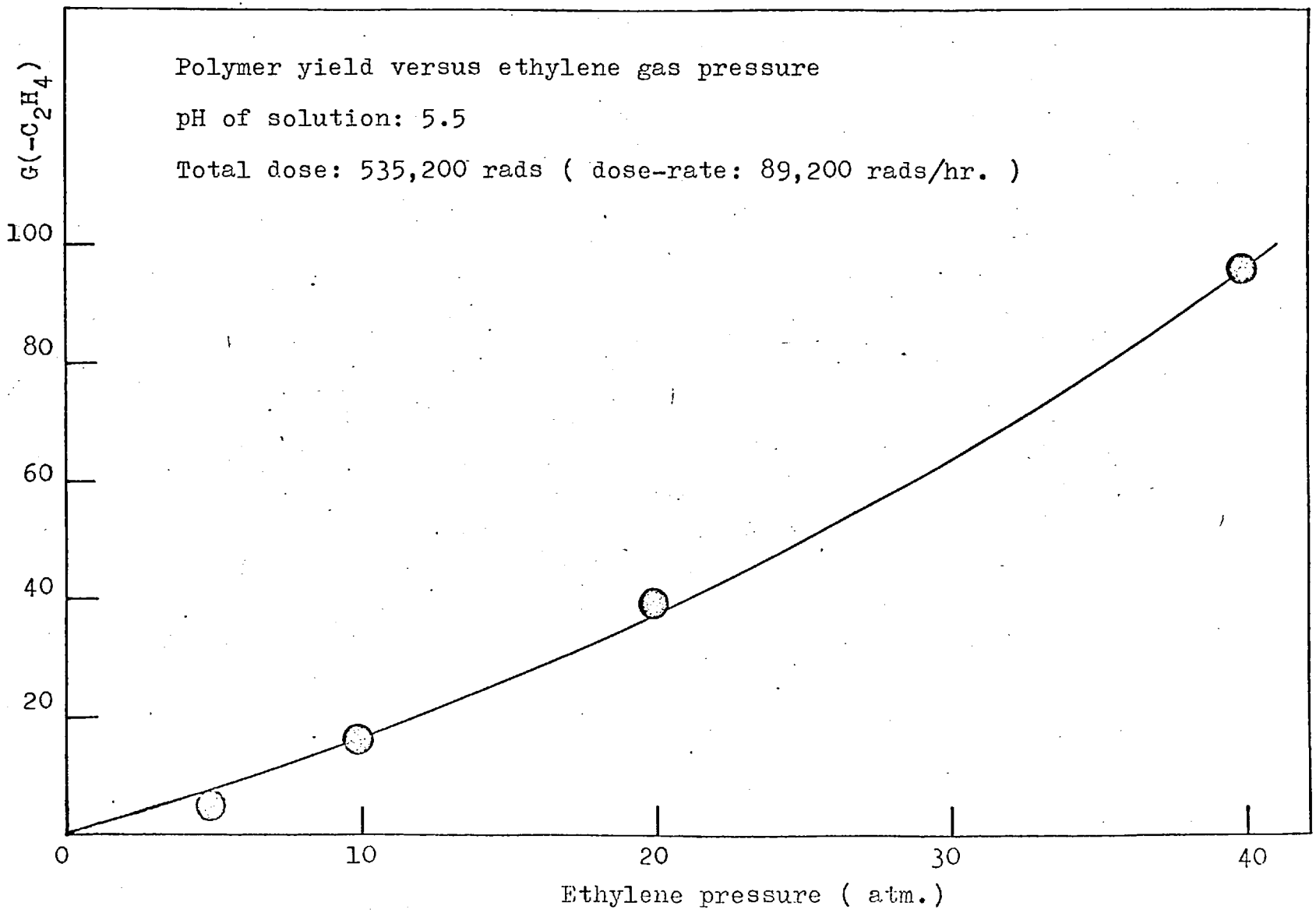

Polymer yield versus ethylene gas pressure
pH of solution: 5.5
Total dose: 535,200 rads (dose-rate: 89,200 rads/hr.)
G(-C2H4)
100
80
60
40
20
0
10
20
30
40
Ethylene pressure (atm.)

Figure 5.

white particles increased until a thick scum was clearly visible just below the surface. On these occasions, the solutions were well stirred, and the weight of polymer in two or three representative samples of the solution was determined until good agreement was obtained ($\pm$ 3%).

The solid polymer samples obtained from these solutions were suitable for investigation by infra-red spectroscopy. Group absorption frequencies corresponding to C-H stretching vibrations (2900 - 2845 $cm.^{-1}$), C-H deformation vibrations (1450 - 1365 $cm.^{-1}$) and skeletal vibrations (770, 710 - 700 $cm.^{-1}$) were observed and correlated with the spectra of alkanes. There was again no evidence for the presence of oxygenated groups, which strongly suggests that the samples are essentially pure polyethylene.

(b) Formation of aldehydes

Acetaldehyde was the only detectable aldehyde produced at low doses, i.e., below 10^5 rads, and its yield was found to be independent of ethylene concentration over the pressure range investigated (Table 7).

At higher doses, the formation in the irradiated solution of other aldehydes, such as n-butyraldehyde, was confirmed (see sub-section 3(b)). The total aldehyde content of the solution was again independent of ethylene concentration up to a total dose of ca. 5×10^5 rads (Table 8).

TABLE 7

Irradiation of aqueous ethylene solutions at pH 5.5 (dose-rate : 89,200 rads/hr.)

Dose-range : 0 - 111,500 rads

Ethylene Pressure(atm.)	Temp.(°C.)	G(CH_3CHO)	G(H_2O_2)
10.0	21.5	0.23	0.67
20.0	19.7	0.22	0.65
40.0	21.0	0.23	0.71

TABLE 8

Irradiation of aqueous ethylene solutions at pH 5.5 (dose-rate : 89,200 rads/hr.)

Dose range : 0 - 490,600 rads

Ethylene Pressure(atm.)	Temp.(°C.)	G(total aldehyde)
10.0	22.0	0.26
20.0	21.7	0.28
40.0	21.6	0.28

(c) Formation of hydrogen peroxide

It can be seen from the corresponding yields for the pressure range 10 to 40 atm. of ethylene (Table 7) that the formation of hydrogen peroxide in the irradiated solution is, like that of acetaldehyde, independent of ethylene concentration.

3. Effect of dose

(a) Formation of polymer

Analysis of the bulk irradiated solution shows that the polymer yield increases linearly with dose (Figure 6). The corresponding G-values for the polymer yield are given in Table 9.

The yields are expressed in terms of the overall G value (molecules of monomer polymerised per 100 eV absorbed). This value which is based on the total energy absorbed in the solution from initiation of the experiment to time, t, is calculated as follows:

$$\text{Overall } G = \frac{W_p \times N \times C}{M.W. \times I \times t}$$

W_p = weight of polymer formed in irradiated solution at time, t, converted to gm./ml.

N = Avogadro's number, 6.023×10^{23} molecules/mole.

I = radiation intensity, rads/hr. (1 rad/hr = 100 ergs/gm.hr.)

t = time from initiation of experiment, hrs.

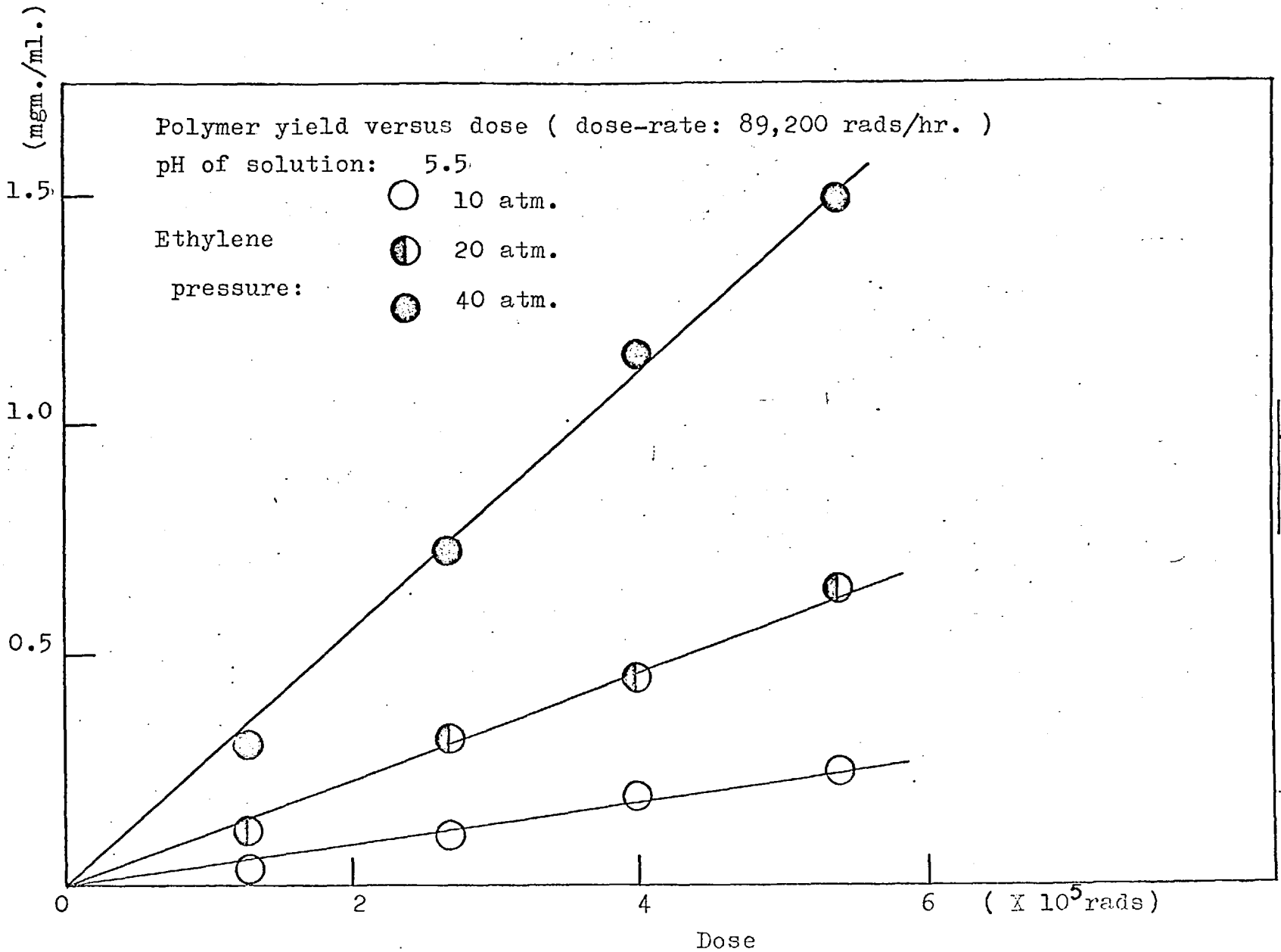

Polymer yield versus dose (dose-rate: 89,200 rads/hr.)
pH of solution: 5.5
Ethylene pressure:
10 atm.
20 atm.
40 atm.
(mgm./ml.)
1.5
1.0
0.5
0
2
4
6
(X 10^5 rads)
Dose

Figure 6.

TABLE 9

Polymer formation in aqueous ethylene solutions at pH 5.5 (dose-rate : 89,200 rads/hr.)

Dose range : 0 - 535,200 rads

Ethylene Pressure(atm.)	G ($-C_2H_4$)
10.0	15.50
20.0	39.22
40.0	95.50

C = conversion factor, 1.602×10^{-12} ergs/eV

M.W.= molecular weight of ethylene, 28.05

(b) Formation of aldehydes

The variation of acetaldehyde yield with total dose is shown in Figures 7 and 8. The yield increases linearly with dose up to about 3×10^5 rads. Beyond this point, other aldehydes can be detected in the irradiated solutions. These include two long-chain aldehydes (with R_F values of 0.8 and 0.9 respectively - see Table 3),which are found in the irradiated solutions at a dose of ca. 5×10^5 rads. These latter compounds probably contain from 6 to 12 carbon atoms[104]. Since further indentification by paper chromatography was not possible at this dilution, individual aldehyde products were not estimated for total doses greater than 3×10^5 rads. The total aldehyde yield was therefore calculated for the irradiated solutions and expressed as a function of the total dose (Figure 9).

(c) Formation of hydrogen peroxide

Measurements on the bulk irradiated solutions show that a linear dependence of the hydrogen peroxide yield or dose up to 10^5 rads (Figure 7 and 8). The corresponding G values for hydrogen peroxide formation in the solution at a pH of 5.5 are given in Table 7.

(d) Other products

The irradiated solutions were also examined

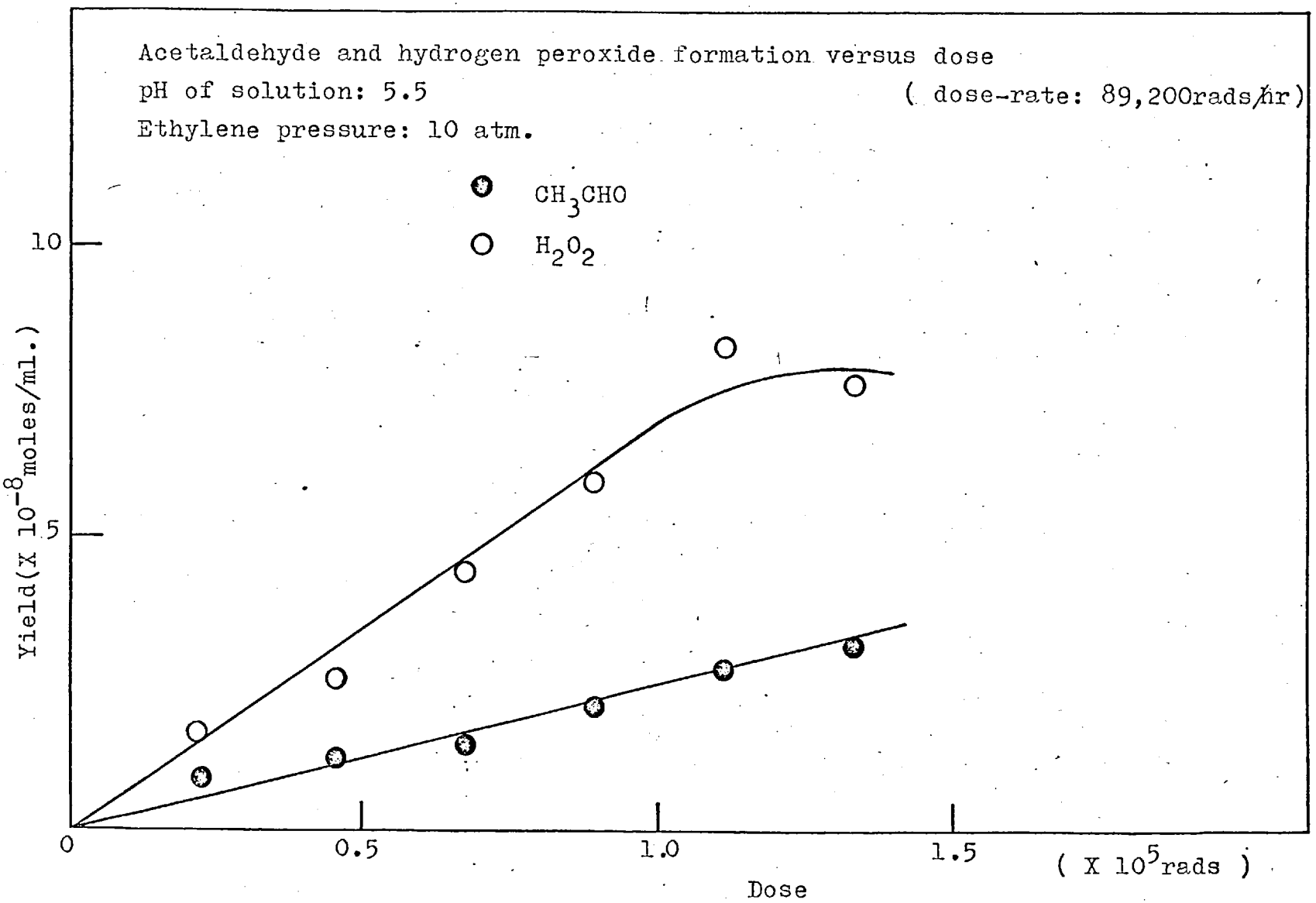

Acetaldehyde and hydrogen peroxide formation versus dose
pH of solution: 5.5
(dose-rate: 89,200rads/hr)
Ethylene pressure: 10 atm.
CH_3CHO
H_2O_2
Yield(X 10^{-8}moles/ml.)
10
5
0
0.5
1.0
1.5
(X 10^5rads)
Dose

Figure 7.

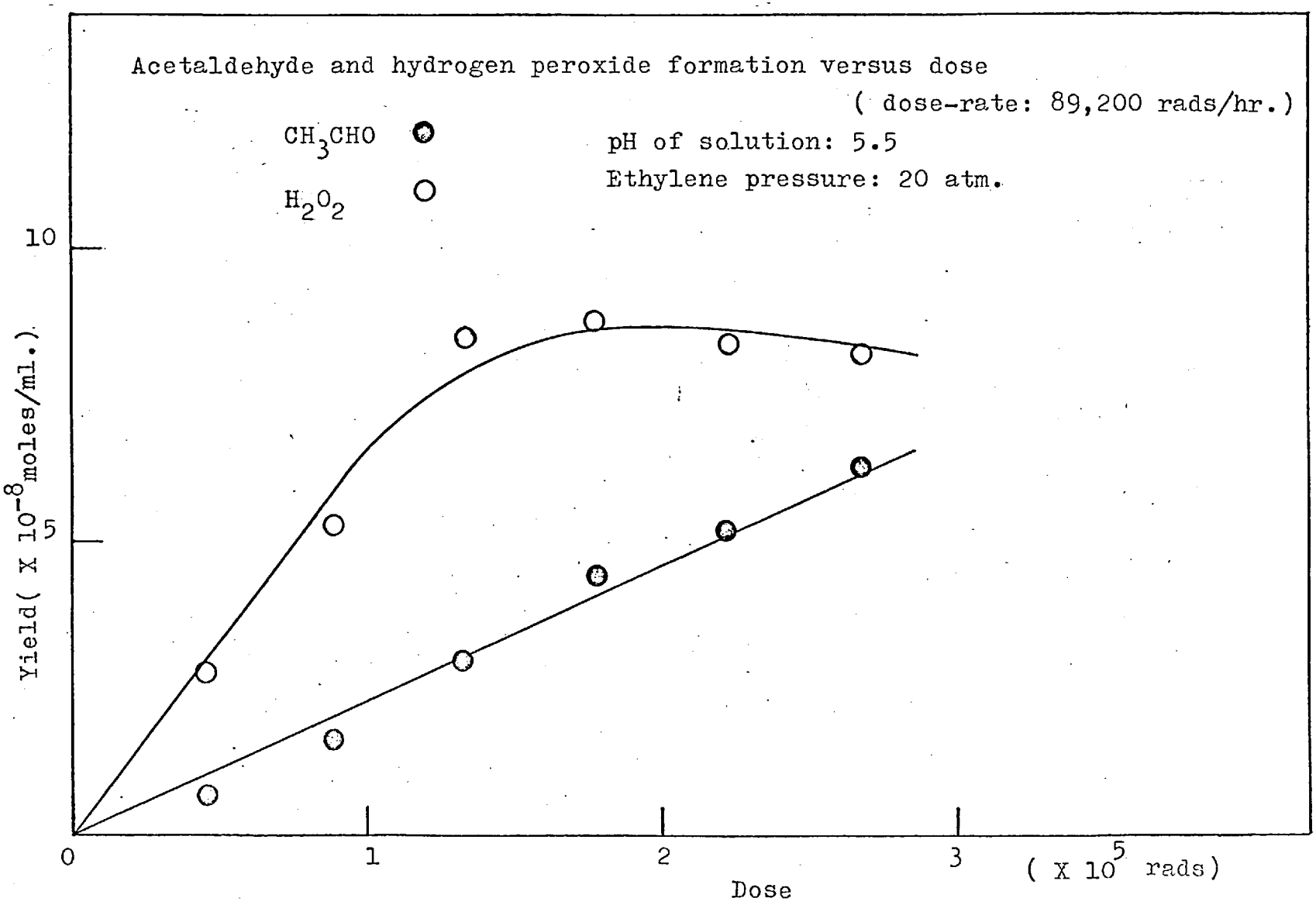

Acetaldehyde and hydrogen peroxide formation versus dose
(dose-rate: 89,200 rads/hr.)
CH_3CHO
H_2O_2
pH of solution: 5.5
Ethylene pressure: 20 atm.
Yield(X 10^{-8} moles/ml.)
10
5
0
1
2
3
Dose
(X 10^5 rads)

Figure 8.

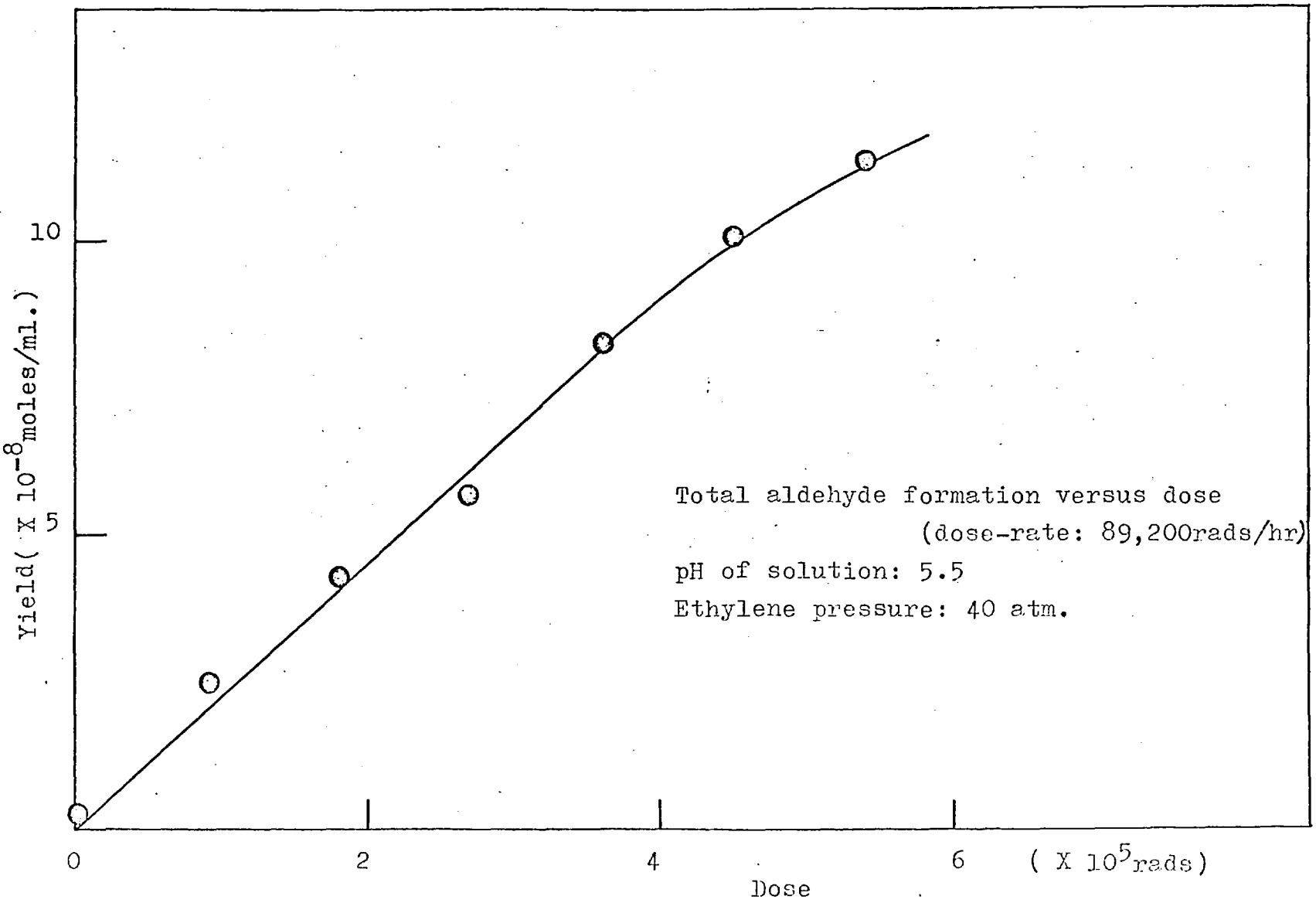

Yield(X 10^{-8} moles/ml.)
10
5
0
2
4
6
(X 10^{5} rads)
Dose
Total aldehyde formation versus dose
(dose-rate: 89,200rads/hr)
pH of solution: 5.5
Ethylene pressure: 40 atm.

Figure 9.

for other products, notably organic acids or alcohols. No organic acids could be detected showing that the G-value for their formation is certainly less than 0.05. On the other hand, small amounts of primary alcohols were found, although the quantity present corresponds to a G value of not more than 0.3.

4. Effect of medium

(a) pH of the solution

(i) Formation of polymer

The weight of polymer obtained from the irradiated solution at pH values of 5.5 and 1.2 are compared in Figure 10. The corresponding G value for polymer formation in 0.1N sulphuric acid at an ethylene pressure of 20 atm. is $G(-C_2H_4) = 79.20$.

(ii) Formation of aldehydes

At a pH of 1.2, the total aldehyde content of the irradiated solutions was found to be equivalent to G (total aldehyde) = 0.55 over the dose-range 0 - 1.4×10^5 rads (ethylene pressure: 20 atm.) Acetaldehyde and n-butyraldehyde are the major aldehydic products. A single long-chain aldehyde was detected in this instance as a trace product on the paper at $R_F = 0.93$, which probably corresponds to a compound with ca.14 carbon atoms. However, if the comparatively small contribution of this compound to the total aldehyde concentration is neglected,

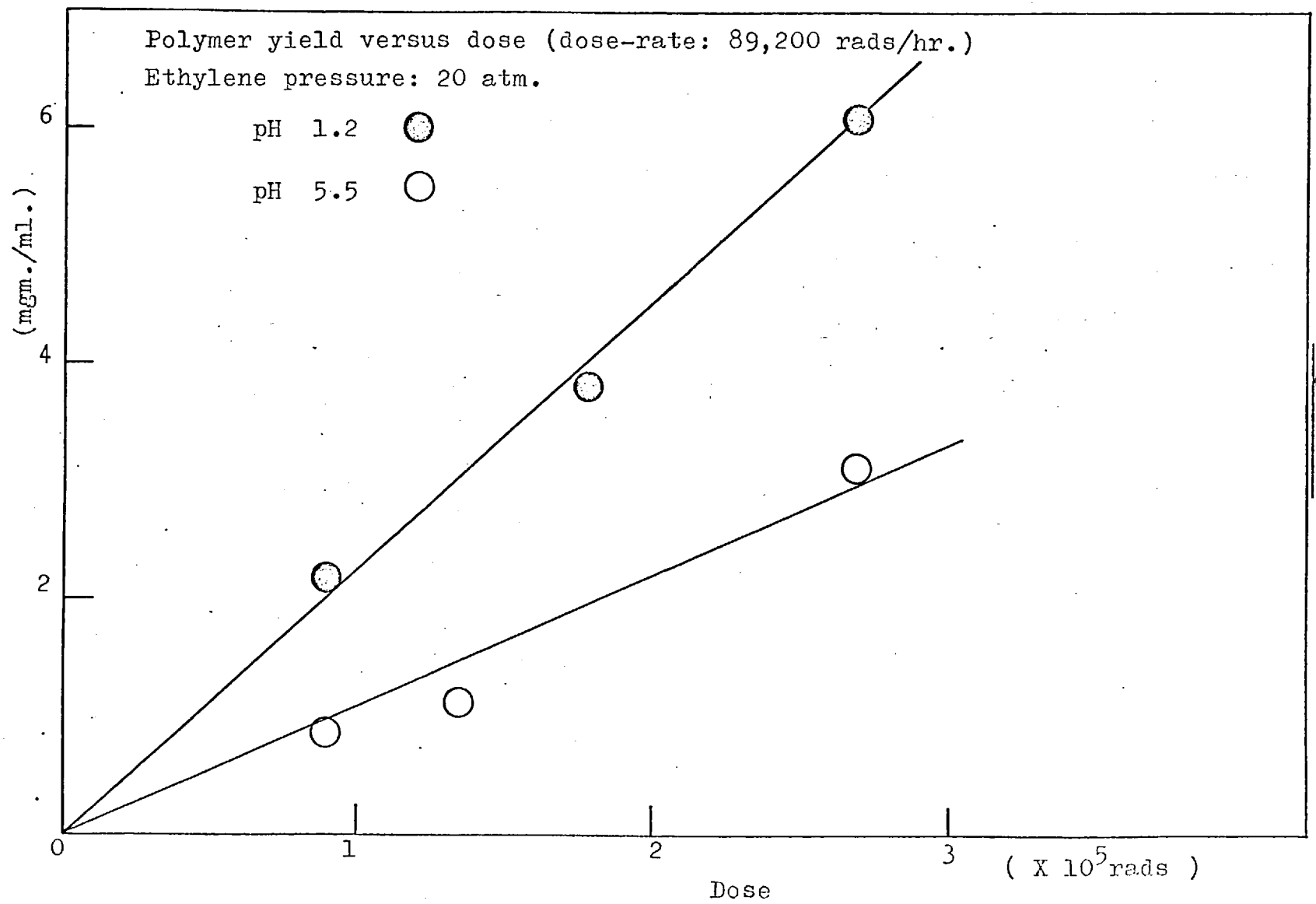

Polymer yield versus dose (dose-rate: 89,200 rads/hr.)
Ethylene pressure: 20 atm.
pH 1.2
pH 5.5
(mgm./ml.)
6
4
2
0
1
2
3
Dose
(X 10^5rads)

Figure 10.

the calculated yields of acetaldehyde and n-butyraldehyde are : $G(CH_3CHO) = 0.39$, $G(CH_3(CH_2)_2CHO) = 0.16$. The dose-yield curves for these products are shown in Figure 11. Direct comparison with the results obtained at a pH of 5.5 (Figure 8) show that the amounts of aldehydes are invariably greater under more strongly acid conditions.

(iii) Formation of hydrogen peroxide

The hydrogen peroxide yields are in contrast lower at a pH of 1.2 than the values obtained in neutral solution (Figure 8). Some typical results are shown Figure 11 and these correspond to : $G(H_2O_2) = 0.42$.

(b) Addition of other species

(i) Irradiations in the presence of ferric ions

Ethylene solutions at a pH of 1.2 were irradiated under a gas pressure of 20 atm. and in the presence of ferric ammonium sulphate to a total dose of 1.3×10^5 rads. The irradiations were carried out without sampling of the solution under pressure, due to the possibility of contamination of the inside surfaces of the sampling valve.

After irradiation, it was noticed that a very small amount of polymerisation had taken place in the solutions, but no estimate of the polymer yield was possible at this stage of the reaction.

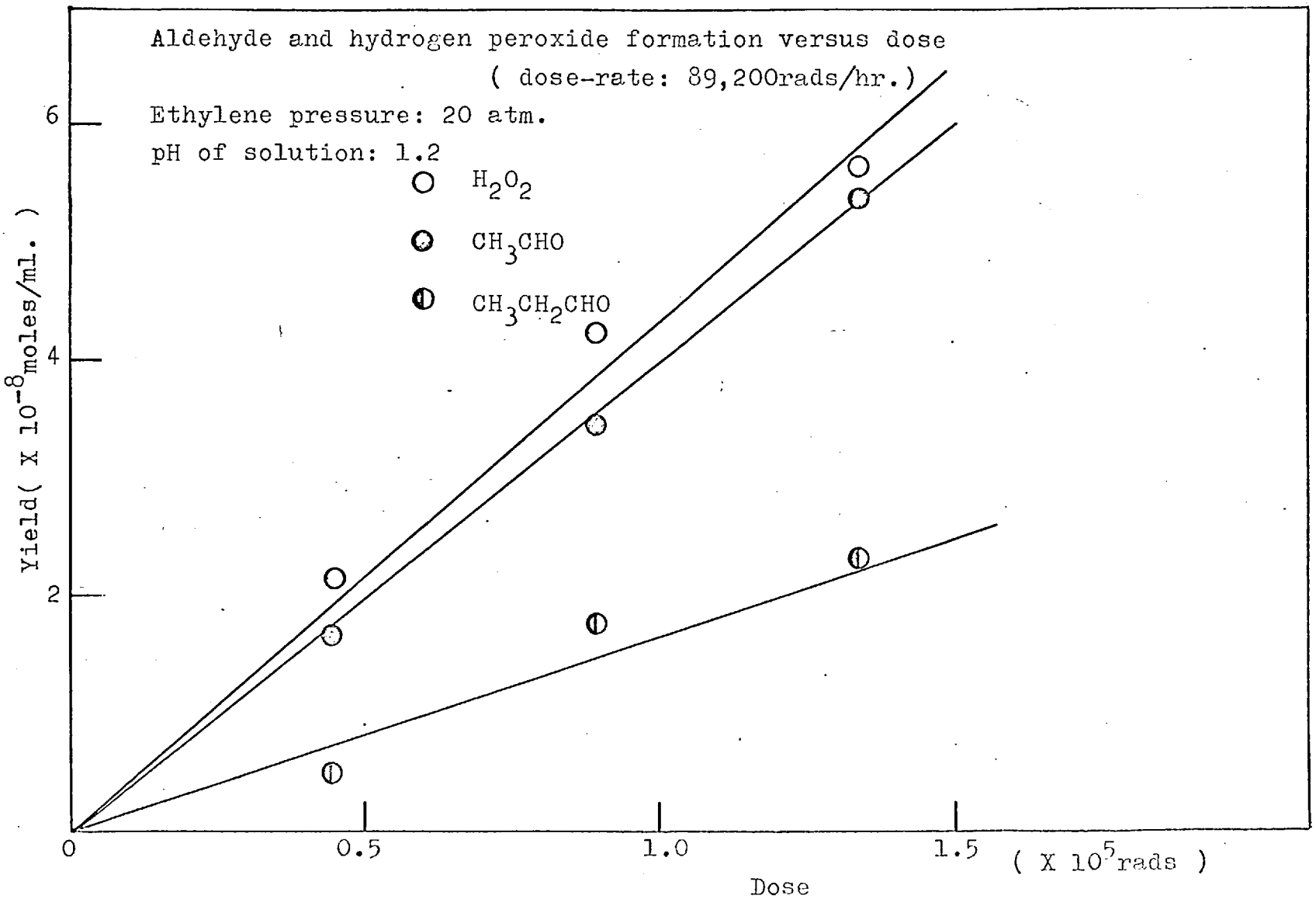

Aldehyde and hydrogen peroxide formation versus dose
(dose-rate: 89,200rads/hr.)
Ethylene pressure: 20 atm.
pH of solution: 1.2
H_2O_2
CH_3CHO
CH_3CH_2CHO
Yield(X 10^{-8}moles/ml.)
6
4
2
0
0.5
1.0
1.5
(X 10^5rads)
Dose

Figure 11.

Acetaldehyde was the most abundant primary aldehydic product. Two long-chain aldehydes could again be detected at about $R_F = 0.9$, and it seems probable that these trace products may have represented an early stage of polymerisation in the solution. The yields recorded in these experiments are given in Table 10.

Hydrogen peroxide oxidises ferrous ions according to the equation:

$$H_2O_2 + Fe^{2+} \longrightarrow Fe^{3+} + OH^- + OH$$

so that measurement of a hydrogen peroxide yield in the irradiated solutions is precluded.

(ii) Irradiations in the presence of hydrogen peroxide

Ethylene solutions at a pH of 5.5 were irradiated in the presence of 10^{-3}M hydrogen peroxide; the inhibitor-free peroxide solutions were de-aerated, and then pressurised to 20 atm. with ethylene prior to irradiation.

Samples removed from the pressure capsule during the irradiation showed evidence of polymerisation in the solution. Although quantitative measurements could not be made, spectrophotometric determination of the extent of light scattering by the polymer particles in suspension showed a linear build-up of the polymer with dose.

The concentration of hydrogen peroxide in the irradiated solution decreased very sharply however with

TABLE 10

Irradiation of aqueous ethylene solutions (20 atm., pH 1.2) in the presence of ferric ions (dose-rate : 89,200 rads/hr.)

Dose-range : 0 - 133,800 rads

Product	Concentration of Fe^{3+}	
	10^{-3}M	10^{-2}M
$G(CH_3CHO)$	0.81	1.07
$G(Fe^{2+})$	3.03	5.50

increasing dose (Figure 12). The G-values for consumption of hydrogen peroxide with total dose absorbed in the solution are given in Table 11.

The total aldehyde yield varied linearly with dose up to 1.2×10^5 rads (Figure 13). Over this dose-range, G (total aldehyde) = 2.50. The individual aldehyde yields were calculated as G(HCHO) = 1.99, $G(CH_3CHO)$ = 0.17 and $G(CH_3CH_2CHO)$ = 0.35. At lower doses (up to 20,000 rads), it was possible to detect a long-chain aldehyde on the paper at R_F = 0.9, and this again would seem to indicate an intermediate stage of polymerisation in the solutions. The individual aldehyde products could not be estimated at these doses due to a lack of specificity in the method of analysis.

The agreement between aldehyde yields determined in separate experiments was in the region of $\pm 4\%$. However, in the case of hydrogen peroxide uptake, the reproducibility was better than 1%.

B. Aqueous solutions of ethylene in the presence of oxygen

1. Introduction

In a general investigation of oxygen-containing systems, a wide variety of experiments was carried out under a range of reactant gas pressures and total dose conditions similar to those used in the experiments in the absence of oxygen. Series of irradiations were carried out on

Figure 12.

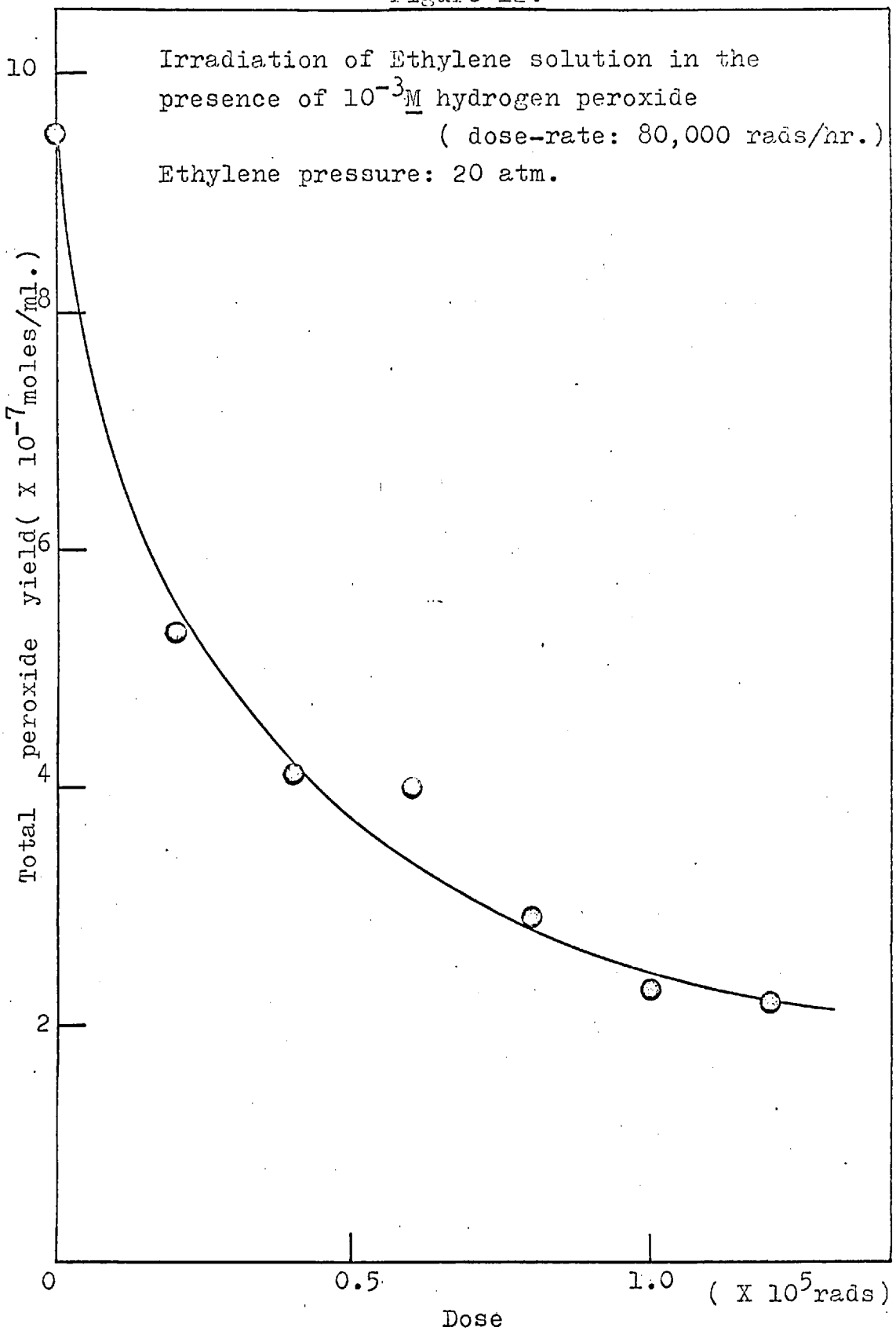

Irradiation of Ethylene solution in the
presence of 10^{-3}M hydrogen peroxide
(dose-rate: 80,000 rads/hr.)
Ethylene pressure: 20 atm.
Total peroxide yield(X 10^{-7}moles/ml.)
10
8
6
4
2
0
0.5
1.0
(X 10^{5}rads)
Dose

TABLE 11

Irradiation of 10^{-3}M hydrogen peroxide solution containing ethylene under pressure (20 atm.)

Dose-rate : 80,000 rads/hr
(Samples of irradiated solution diluted x 25 before analysis)

Dose ($\times 10^4$ rads)	O.D.$_{350m\mu}$ (1cm. cells)	$[H_2O_2]$ ($\times 10^{-4}$M)	$G(-H_2O_2)$
0	0.965	0.95	
2	0.538	0.53	20.3
4	0.420	0.41	12.9
6	0.405	0.40	8.9
8	0.294	0.29	8.0
10	0.234	0.23	6.9

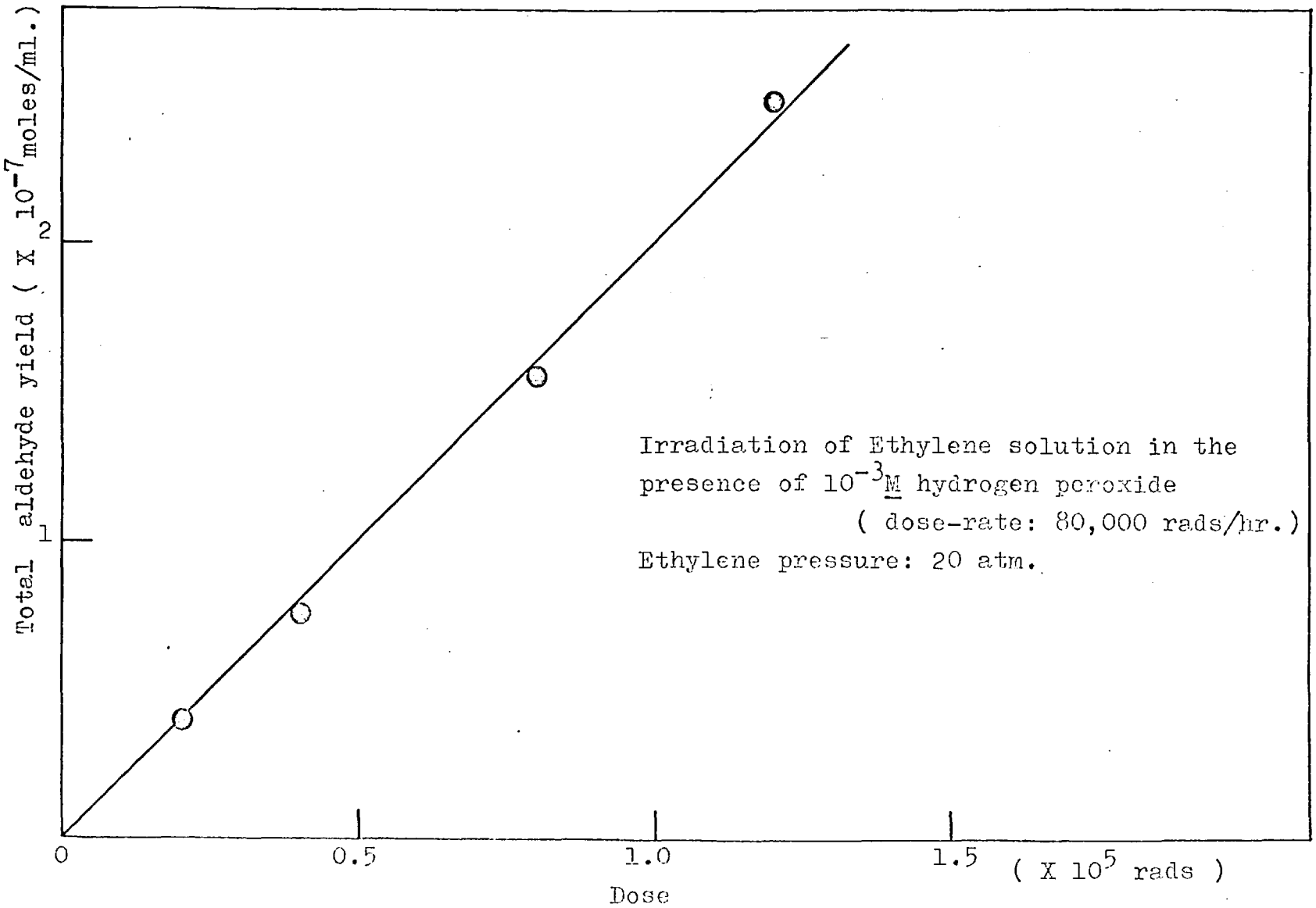

Total aldehyde yield (X 10⁻⁷ moles/ml.)
2
1
0
0.5
1.0
1.5
(X 10⁵ rads)
Dose
Irradiation of Ethylene solution in the
presence of 10⁻³ M hydrogen peroxide
(dose-rate: 80,000 rads/hr.)
Ethylene pressure: 20 atm.

Figure 13.

ethylene-oxygen solutions equilibrated with 1% and 10% oxygen gas-mixtures respectively. In addition, the effect was studied of increasing the oxygen concentration in the solution at a constant ethylene concentration.

The polymerisation process is inhibited in the oxygenated solutions, but starts again once all the oxygen is removed. The yield and number of aldehydic products are however substantially increased by the presence of oxygen. The total peroxide yield is also found to be significantly higher under these conditions.

2. Effect of total pressure of a given gas mixture

After equilibration with the gas mixture at a particular total pressure, the solution of the reactant gases was irradiated at a dose-rate of ca. 9×10^4 rads/hr. Investigations over the range 10 to 40 atm. for both the 1% and 10% oxygen mixtures showed relatively little effect of total pressure on the measured product yields (Tables 12 and 13).

3. Effect of dose

(a) Formation of aldehydes

Analysis of samples removed from the pressure vessel during irradiation of solutions equilibrated with the 1% oxygen mixture showed that the individual aldehyde yield-dose curves are initially linear (Figure 14). A stage is reached during the irradiation however when the relatively

TABLE 12

Irradiation of solutions equilibrated at pH 5.5 with ethylene-oxygen (1%) mixtures at different pressures (dose-rate : 89,200 rads/hr.)

Dose-range : 0 - 89,200 rads

Total pressure (atm.)	G(HCHO)	G(CH_3CHO)	G(CH_3CH_2--CHO)	G(H_2O_2)	G(ROOH)
10	0.15	1.03	0.32	0.64	1.56
20	0.20	1.04	0.39	0.69	1.81
40	0.22	1.18	0.43	0.48	2.12

TABLE 13

Irradiation of solutions equilibrated at pH 5.5 with ethylene-oxygen (10%) mixtures at different pressures (dose-rate : 89,200 rads/hr.)

Dose-range : 0 - 89,200 rads

Total pressure (atm.)	G(HCHO)	G(CH_3CHO)	G(CH_3CH_2-CHO)	G(H_2O_2)	G(ROOH)
10	0.34	2.32	0.64	0.59	4.14
20	0.54	2.00	0.73	0.80	4.02
40	0.37	2.15	0.71	0.76	3.74

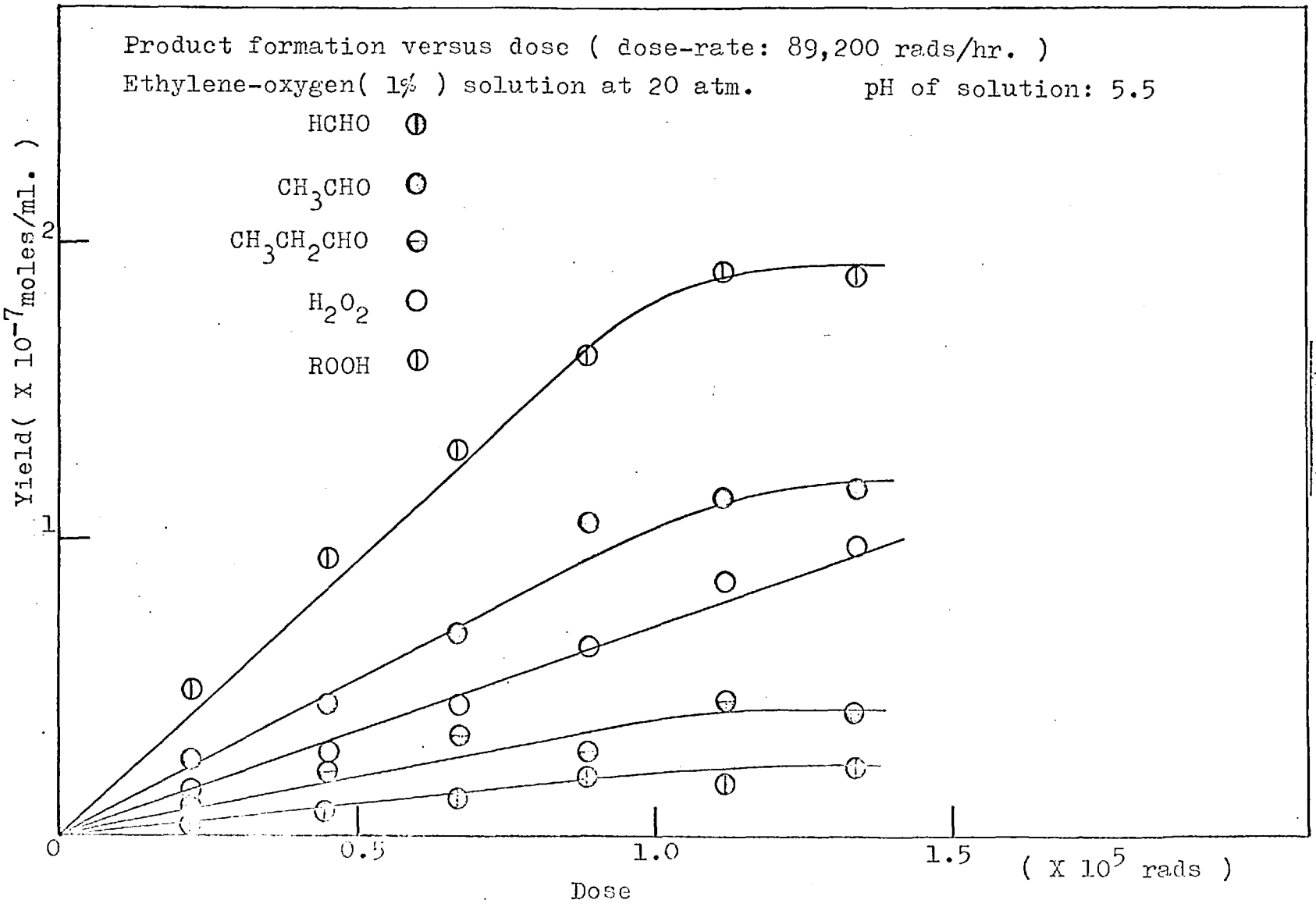

Product formation versus dose (dose-rate: 89,200 rads/hr.)
Ethylene-oxygen(1%) solution at 20 atm.
pH of solution: 5.5
HCHO
CH_3CHO
CH_3CH_2CHO
H_2O_2
ROOH
Yield(X 10^{-7} moles/ml.)
2
1
0
0.5
1.0
1.5
(X 10^5 rads)
Dose

Figure 14.

small amount of oxygen in the original solution has been fully consumed in the radiation-induced reactions. It is at this oxygen "break-point" that analysis of the samples shows a marked decrease in the yield per unit dose. At higher total pressures with respect to the mixture, the oxygen concentration in the solution is proportionally increased so that the irradiations may be extended to higher doses. Diffusion from the gas phase into the solution is a relatively slow process, so that once all the oxygen present initially has been consumed, the reaction proceeds virtually as in the absence of oxygen.

Solutions irradiated in equilibrium with the 10% oxygen mixture also show a strong linear dependence on dose (Figure 15). In this instance, as expected the oxygen "break-point" occurs in the solutions at a dose greater than ca. 3×10^5 rads.

The irradiated solutions corresponding to both 1% and 10% oxygen mixtures were examined for the presence of other aldehydic products in addition to those shown in Figures 14 and 15.

In solutions of the 1% mixture, a single long-chain aldehyde was detected at a total dose of ca. 10^5 rads. This compound was probably associated with initiation of polymerisation in the solution in the region of the oxygen "break-point". A dialdehyde-hydrazone was also detected

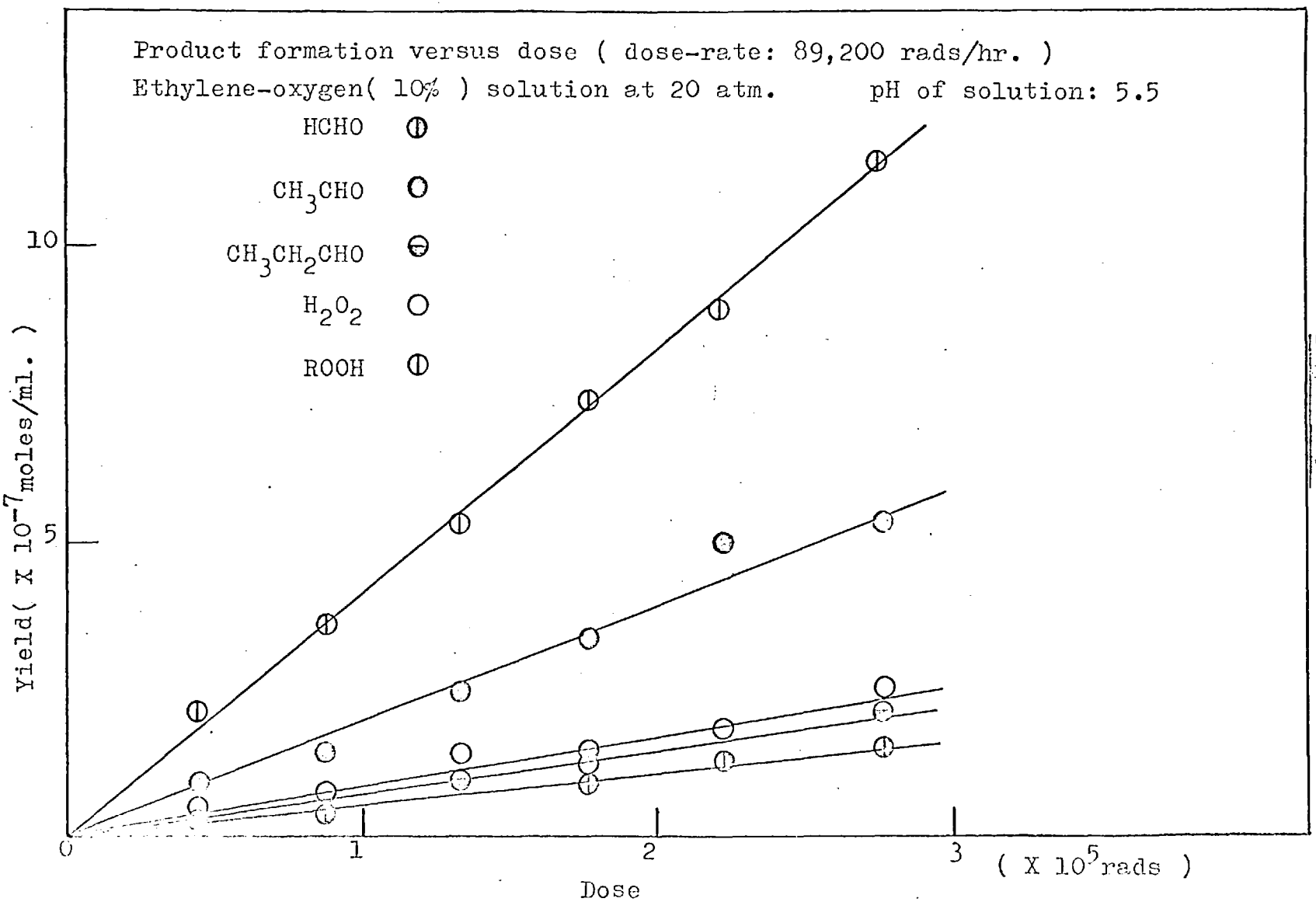

Product formation versus dose (dose-rate: 89,200 rads/hr.)
Ethylene-oxygen(10%) solution at 20 atm.
pH of solution: 5.5
HCHO
CH_3CHO
CH_3CH_2CHO
H_2O_2
ROOH
Yield(X 10^{-7}moles/ml.)
10
5
0
1
2
3
Dose
(X 10^5rads)

Figure 15.

during paper chromatography of the irradiation products. This would seem to indicate the presence in the irradiated solutions of either glyoxal, or glycolaldehyde, which forms the same hydrazone derivative. However, an insufficient quantity of this product was present to allow it to be estimated by the available colorimetric methods of analysis. The G-value for its formation must therefore certainly be less than 0.01, which indicates that this compound is a very minor product of the radiolysis.

Dialdehyde was also detected as a trace product in solutions of the 10% oxygen mixture.

(b) Formation of peroxide products

The concentration of total peroxide in the irradiated solutions equilibrated with both the 1% and 10% oxygen mixtures was also found to increase linearly with dose. The appearance of a relatively high yield of organic hydroperoxide in these solutions was certainly one of the most significant results obtained during this part of the investigation. Hydrogen peroxide was produced simultaneously but in much lower yield (Figures 14 and 15). The identity of the organic hydroperoxide formed in these solutions will be discussed more fully in a later Section.

(c) Other products

Further attempts were made to estimate any other products of the radiolysis using the various methods

previously described, but no positive result was obtained. In particular, no aliphatic acids or alcohols could be detected in the irradiated solutions of either the 1% or the 10% oxygen mixture.

4. Effect of variation of oxygen concentration at a constant ethylene concentration in the solution

Throughout this series of experiments, the ethylene pressure above the solution was maintained at 20 atm.; this corresponds to an ethylene concentration of 0.11M in the solution. The oxygen component of the gas mixture equilibrated with the solution was then varied over the range 2 to 40% of the mixture (0.5 to 13.3 atm.); the corresponding solute concentration was therefore in the range 0.001 to 0.02M with respect to oxygen.

The formation of the individual aldehydic and peroxidic products was followed over the dose-range 0 - 1.2×10^5 rads, using a dose-rate of ca. 8×10^4 rads/hr. Experiments were carried out at pH values of 5.5 and 1.2. In every instance, the product yields varied linearly with dose as shown, for example, in Figures 16 and 17.

(a) Formation of aldehydes

The G values for the formation of the individual aldehydes in the irradiated solutions at pH values of 5,5 and 1.2 are given in Tables 14 and 15 respectively.

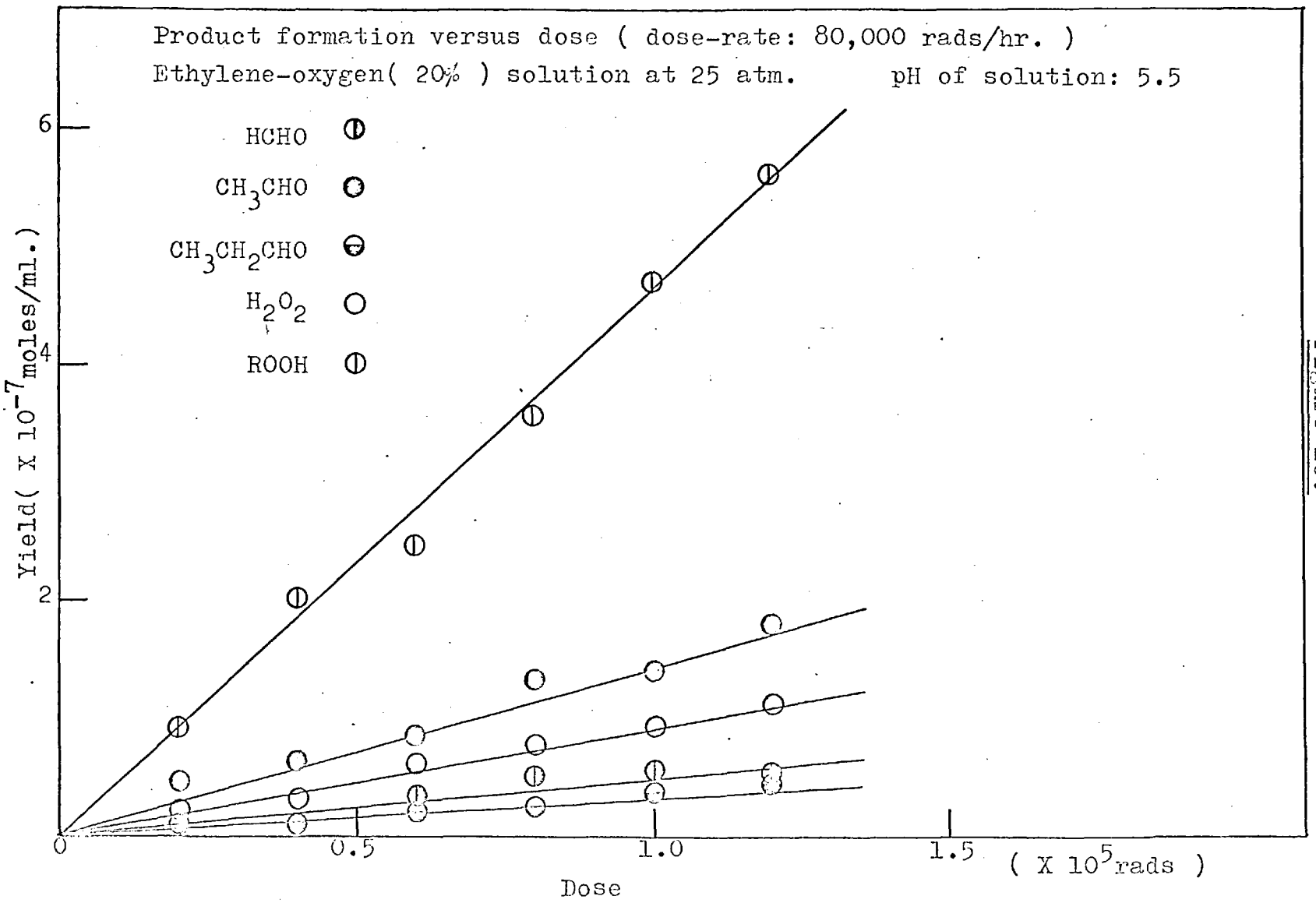

Product formation versus dose (dose-rate: 80,000 rads/hr.)
Ethylene-oxygen(20%) solution at 25 atm.
pH of solution: 5.5
HCHO
CH_3CHO
CH_3CH_2CHO
H_2O_2
ROOH
Yield(X 10^{-7} moles/ml.)
6
4
2
0
0.5
1.0
1.5
(X 10^5 rads)
Dose

Figure 16.

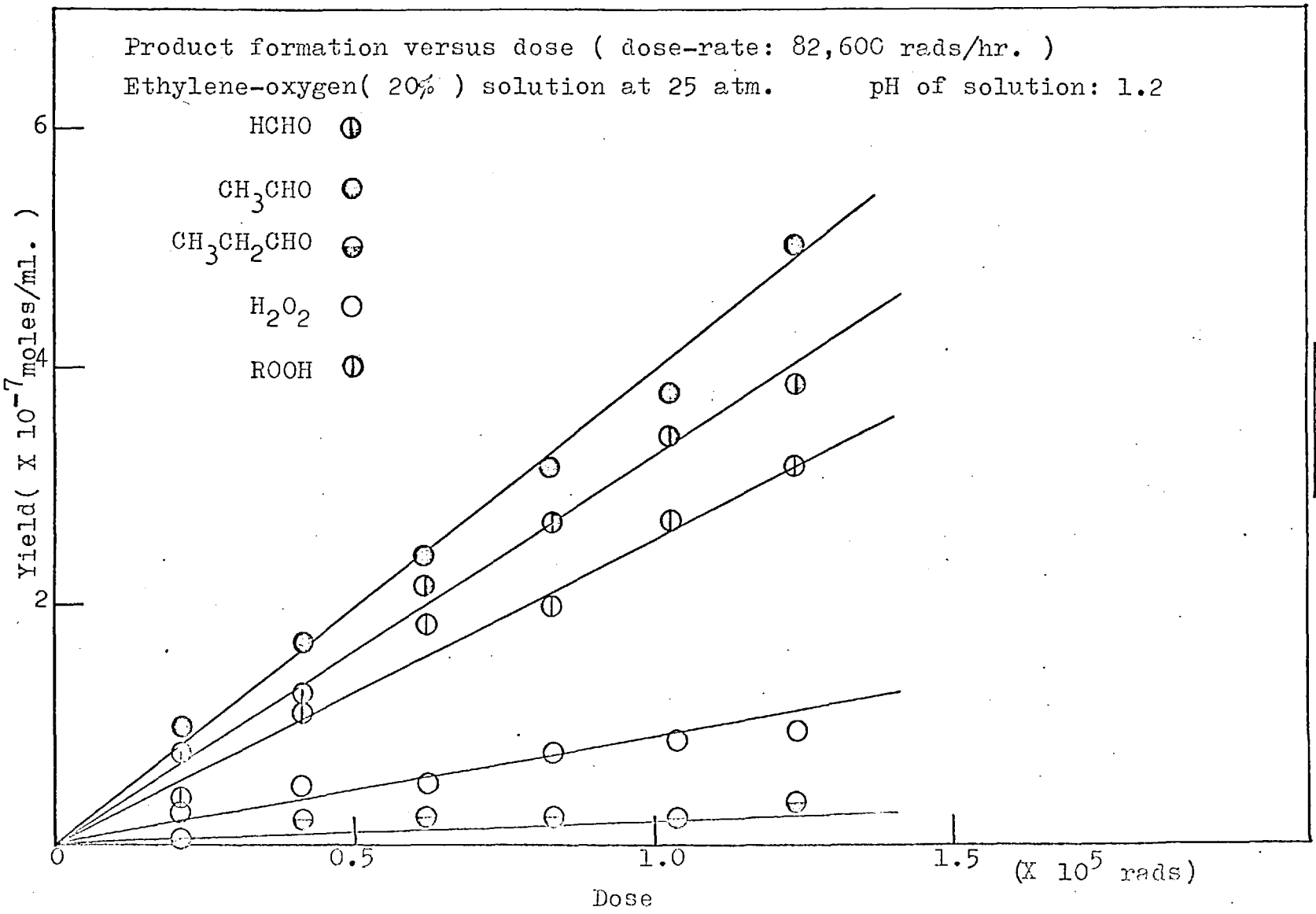

Product formation versus dose (dose-rate: 82,600 rads/hr.)
Ethylene-oxygen(20%) solution at 25 atm.
pH of solution: 1.2
HCHO
CH_3CHO
CH_3CH_2CHO
H_2O_2
ROOH
Yield(X 10^{-7} moles/ml.)
6
4
2
0
0.5
1.0
1.5
(X 10^5 rads)
Dose

Figure 17.

TABLE 14

Irradiation yields from ethylene-oxygen solutions at pH 5.5 (dose-rate : 80,000 rads/hr.)

Dose-range : 0 - 120,000 rads

Average temp. : 19.6°C

Total gas pressure (atm.)	21.0	22.0	23.0	24.0	25.0	33.3
% Oxygen	4.76	9.09	13.04	16.66	20.0	40.0
G(HCHO)	0.65	0.43	0.58	0.53	0.43	0.51
G(CH_3CHO)	2.33	1.98	1.68	1.44	1.37	1.25
G(CH_3CH_2CHO)	0.54	0.75	0.51	0.71	0.33	0.13
G(H_2O_2)	0.30	0.76	1.04	0.62	0.88	1.26
G(ROOH)	4.16	4.74	4.16	4.26	4.48	4.14

TABLE 15

Irradiation yields from ethylene-oxygen solutions at pH 1.2 (dose-rate : 82,600 rads/hr.)

Dose-range : 0 - 123,900 rads

Average temp. : 19.4°C.

Total gas pressure(atm.)	20.5	21.0	22.0	23.0	24.0	25.0	33.3
% Oxygen	2.44	4.76	9.09	13.04	16.66	20.0	40.0
G(HCHO)	0.61	0.59	0.65	0.70	1.31	3.16	2.43
$G(CH_3CHO)$	5.15	5.46	5.29	4.16	3.85	3.82	4.46
$G(CH_3CH_2CHO)$	0.41	0.40	0.25	0.17	0.12	0.16	0.28
$G(H_2O_2)$	1.22	1.08	0.80	0.32	0.30	0.86	0.90
G(ROOH)	2.64	2.69	3.17	4.42	3.75	2.45	3.08

In addition to these products, glycolaldehyde or glyoxal was detected in every case. Due to the exceptionally low G value (less than 0.01), it was not possible to obtain a more accurate estimation using the present methods of analysis. Neither was it possible to distinguish between glycolaldehyde and glyoxal at this concentration.

The variation of G(total aldehyde) with increasing oxygen pressure in the gas mixture is shown in Figures 18 and 19 respectively. At a pH of 5.5, the yield of aldehydic products decreases as the percentage of oxygen in the gas mixture is increased above 10%.

The individual aldehyde yields are also plotted for the different pH values in Figures 20 and 21. Under both sets of conditions, the acetaldehyde yield decreases when the concentration of oxygen in the gas mixture is greater than 5%, but becomes reasonably constant with more than 20% oxygen present. In acid solution, the formaldehyde yield appears to be strongly dependent on oxygen concentration; at the higher concentrations of oxygen, the yield is considerably greater than that in neutral solution.

(b) Formation of peroxide products

The total peroxidic yields measured in the irradiated solutions under the different pH conditions are shown in Figures 18 and 19, and the total aldehyde yields

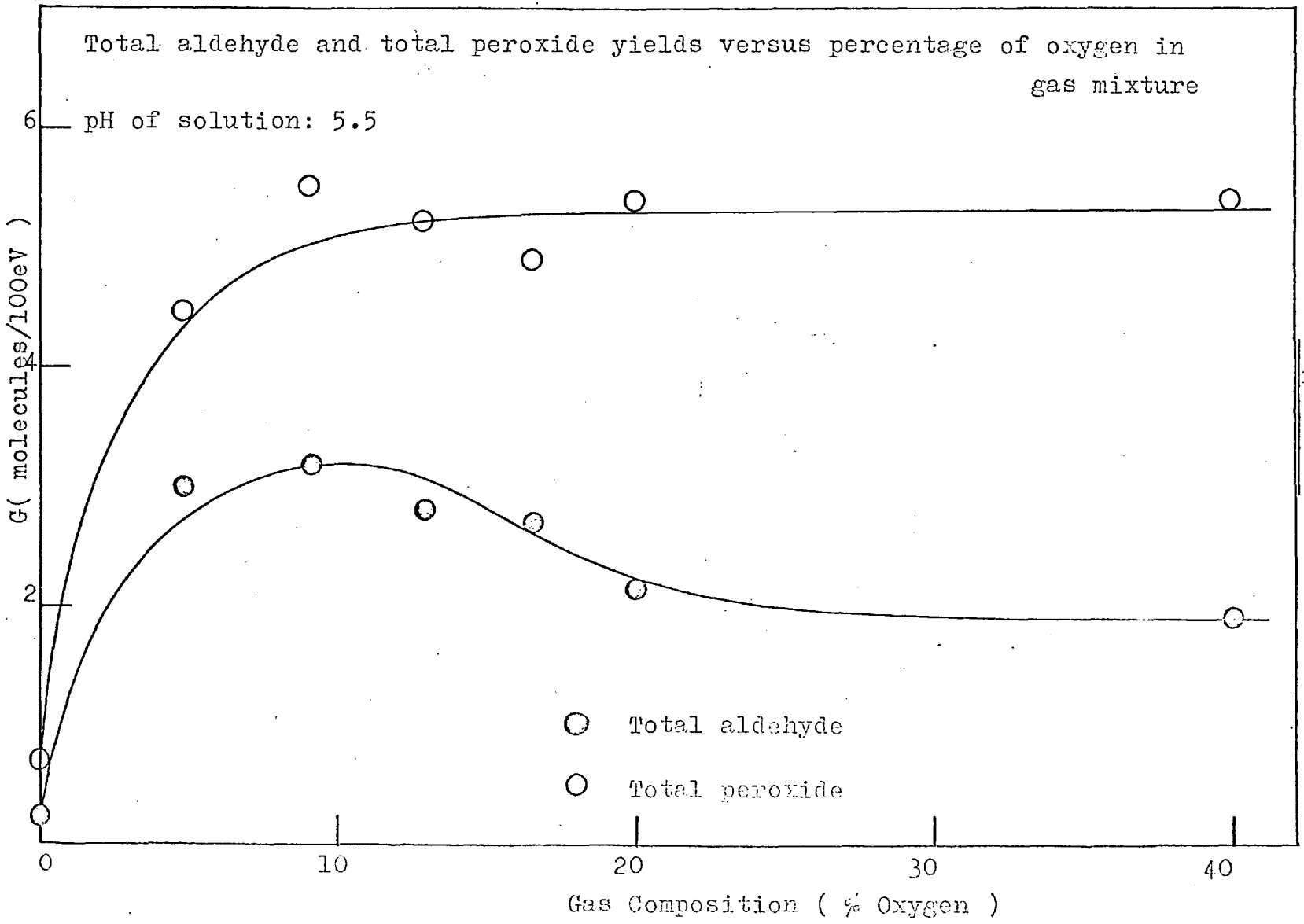

Total aldehyde and total peroxide yields versus percentage of oxygen in gas mixture
pH of solution: 5.5
G(molecules/100eV)
6
4
2
0
10
20
30
40
Gas Composition (% Oxygen)
Total aldehyde
Total peroxide

Figure 18.

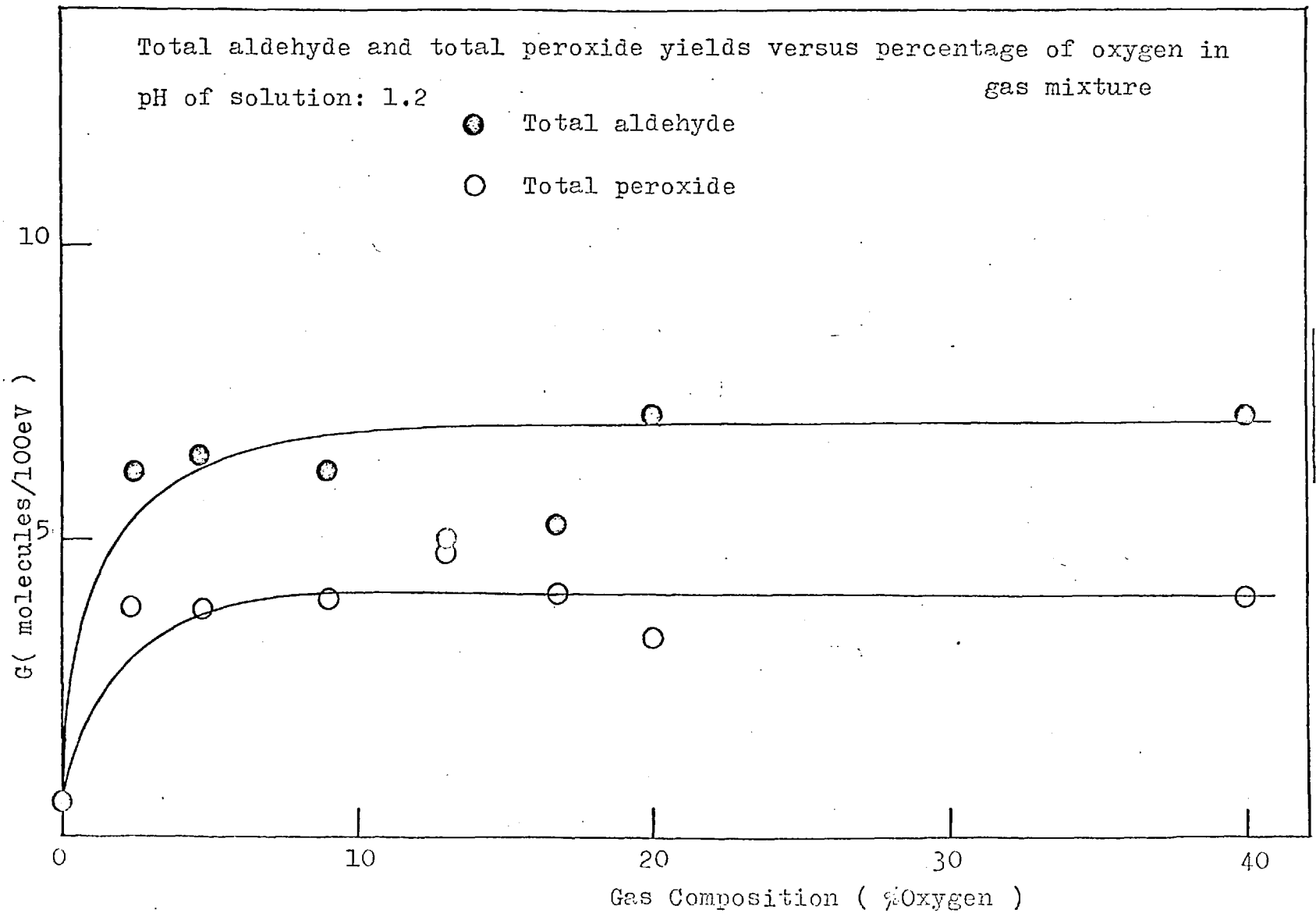

Total aldehyde and total peroxide yields versus percentage of oxygen in gas mixture
pH of solution: 1.2
Total aldehyde
Total peroxide
G(molecules/100eV)
10
5
0
10
20
30
40
Gas Composition (%Oxygen)

Figure 19.

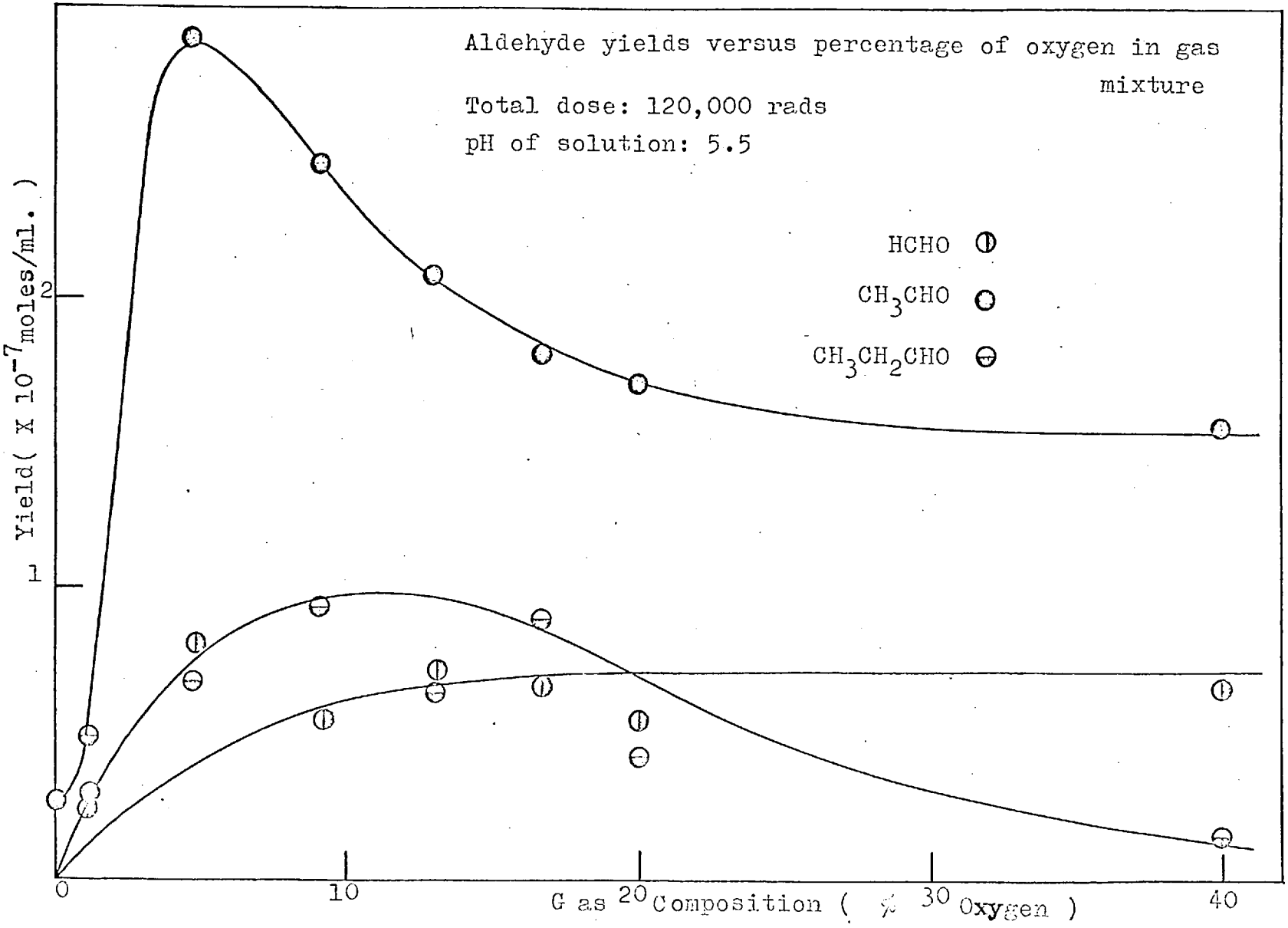

Aldehyde yields versus percentage of oxygen in gas mixture
Total dose: 120,000 rads
pH of solution: 5.5
HCHO
CH_3CHO
CH_3CH_2CHO
Yield (X 10^{-7} moles/ml.)
2
1
0
10
20
30
40
Gas Composition (% Oxygen)

Figure 20.

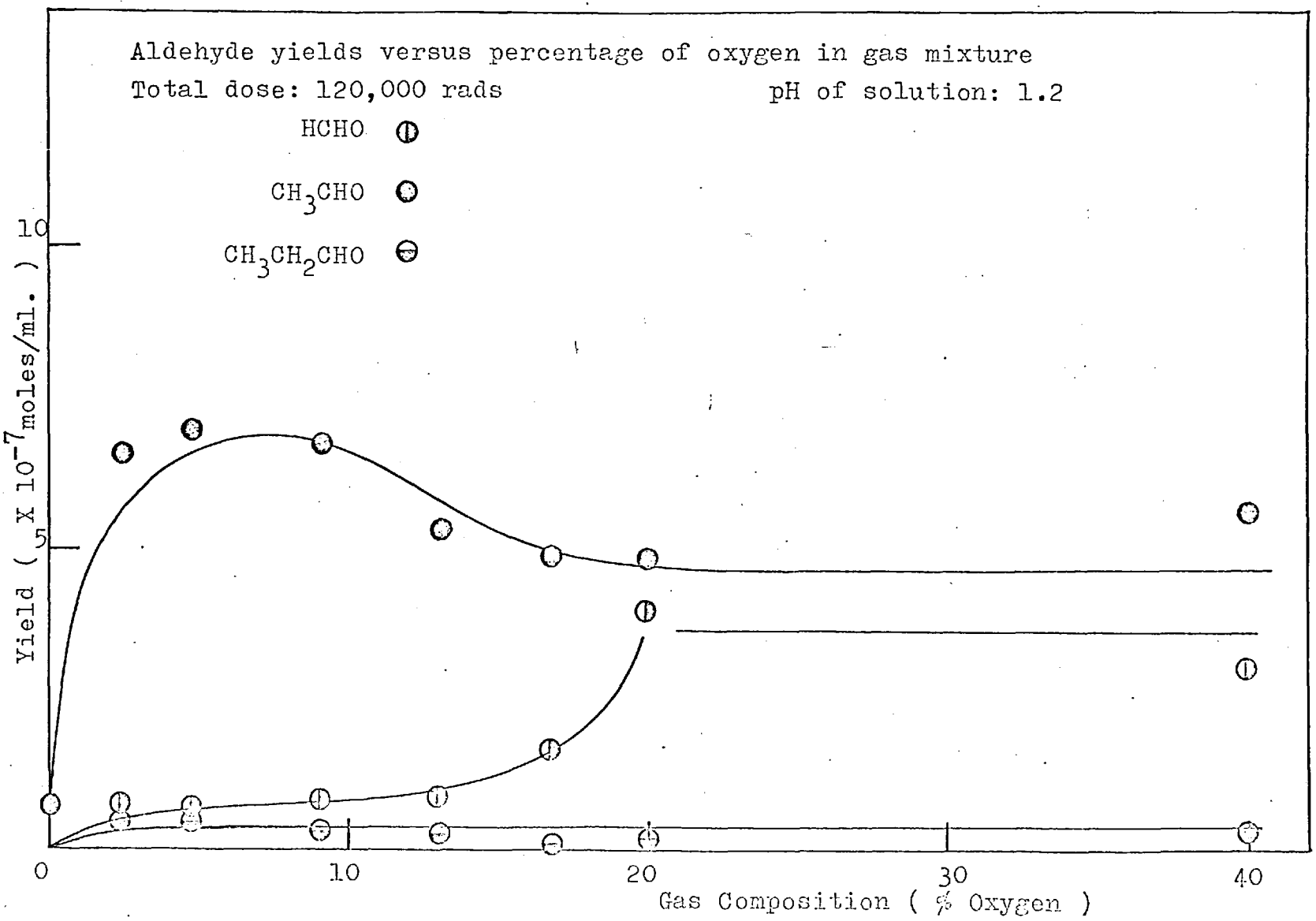

Aldehyde yields versus percentage of oxygen in gas mixture
Total dose: 120,000 rads
pH of solution: 1.2
HCHO
CH_3CHO
CH_3CH_2CHO
Yield ($\times 10^{-7}$ moles/ml.)
10
5
0
10
20
30
40
Gas Composition (% Oxygen)

Figure 21.

are also given for comparison.

Examination of the irradiated solutions indicated the presence of a considerable yield of an organic hydroperoxide over and above that of hydrogen peroxide under both neutral and acid conditions. The yields of the hydroperoxide and of hydrogen peroxide are given separately in Tables 14 and 15.

Immediately oxygen is introduced into the solution, the organic hydroperoxide appears in high yield, and thereafter remains more or less independent of the oxygen concentration (Figures 22 and 23). The highest yields of this product are obtained in neutral solution. The hydrogen peroxide yields, however, appear to be largely independent of the pH of the medium and of the oxygen concentration over the whole range examined.

(c) Identification of the organic hydroperoxide formed in the irradiated solutions

The large yield of stable organic hydroperoxide formed in both neutral and acid solutions is an interesting feature of the present system. It has been stated previously that the action of ionizing radiations on ethylenic compounds in the presence of oxygen can give rise to more or less stable hydroxyhydroperoxides[32]. If this type of peroxide is formed from ethylene, then the most likely compound is β-hydroxyethylhydroperoxide, $CH_2OH.CH_2OOH$.

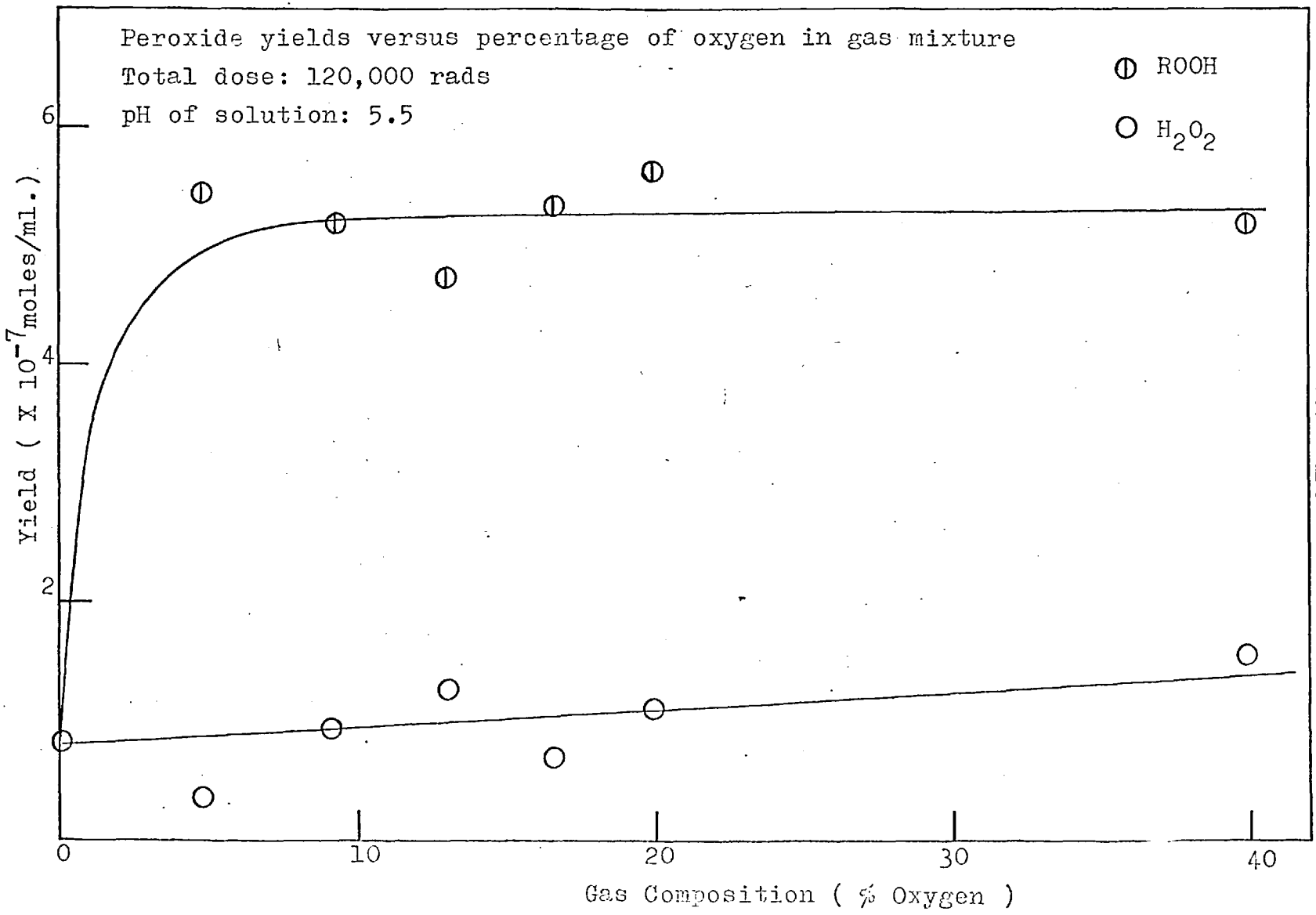

Peroxide yields versus percentage of oxygen in gas mixture
Total dose: 120,000 rads
pH of solution: 5.5
ROOH
H_2O_2
Yield (X 10^{-7} moles/ml.)
6
4
2
0
10
20
30
40
Gas Composition (% Oxygen)

Figure 22.

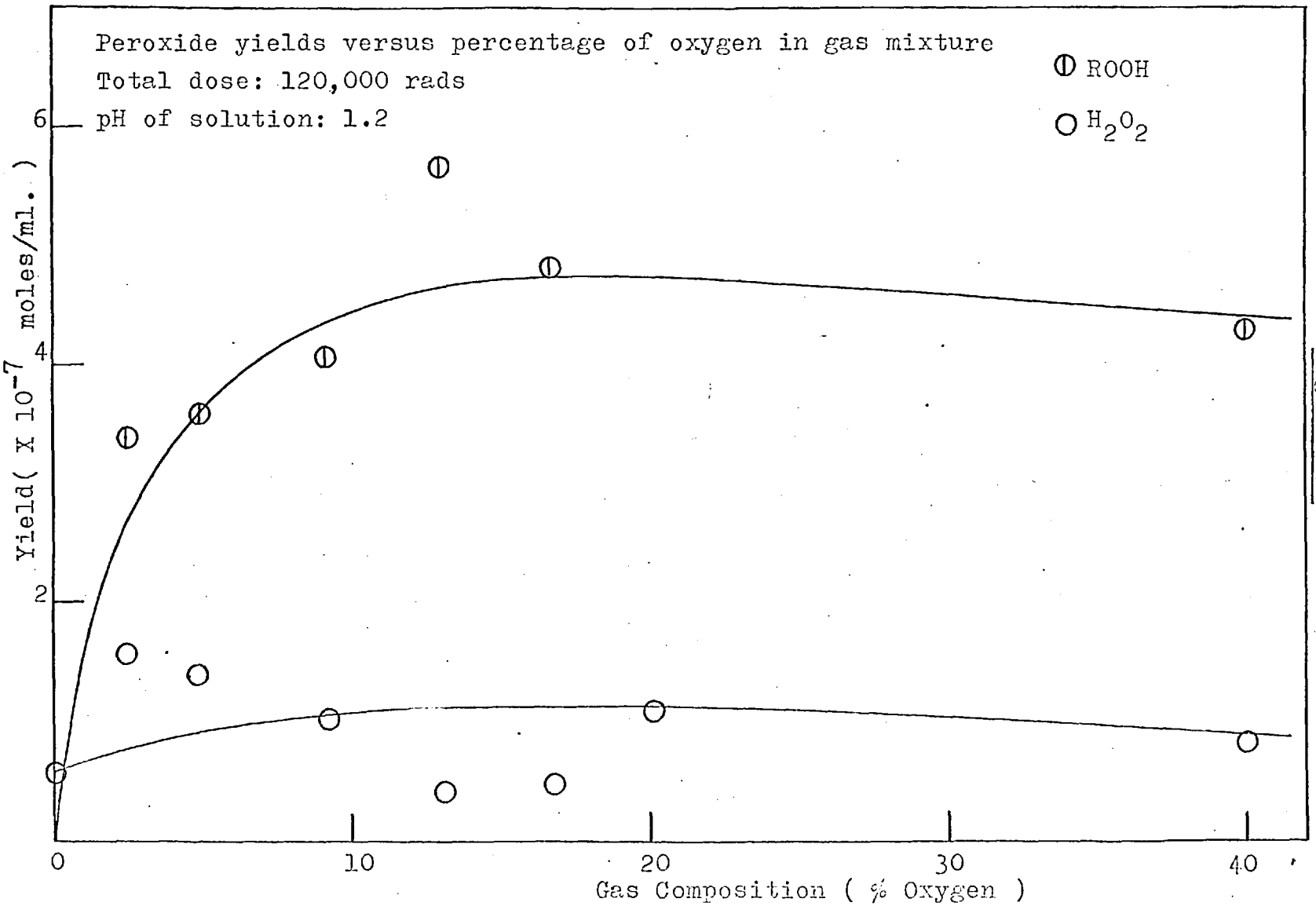

Peroxide yields versus percentage of oxygen in gas mixture
Total dose: 120,000 rads
pH of solution: 1.2
ROOH
H_2O_2
Yield(X 10^{-7} moles/ml.)
6
4
2
0
10
20
30
40
Gas Composition (% Oxygen)

Figure 23.

The existence of this hydroperoxide either in the pure state or in aqueous solution has not been postulated prior to the present investigation. It was necessary, therefore, first to synthesise this peroxide (as described in Section IIB), then to attempt to relate its properties to those of the unidentified hydroperoxide formed in the irradiated ethylene-oxygen solutions.

The rates of oxidation of iodide ions in aqueous solution are found to be characteristic and to some extent diagnostic of the nature of peroxides (Table 16). The reaction in the presence of excess iodide is of the first order, and the rate constant was in this instance determined by application of Guggenheim's method[129] to the optical density versus time curve for the formation of tri-iodide ions.

For the synthetic hydroperoxide, the following procedure was employed.

0.1 ml. of the reaction mixture prepared according to the method already described (Section IIB) were diluted to 50 ml. 0.5 ml. of the dilute solution were then treated successively with 1 ml. of titanium sulphate reagent and 2 - 5 ml. of 6N ammonium hydroxide solution. After the solution had been centrifuged for 5 min. to remove the titanium complex, 1 ml. of the supernatant liquid containing the separated hydroperoxide was mixed with

TABLE 16

Comparison of pseudo-first order specific rate constants for reaction between iodide reagent and hydrogen peroxide, synthetic hydroperoxides and hydroxyhydroperoxides

Compound	$k(sec.^{-1}) \times 10^4$	Ref.
H_2O_2	11.50	130
CH_3OOH	0.80	28
CH_3CH_2OOH	0.27	131
$CH_3.\underset{\displaystyle OOH}{\underset{\displaystyle |}{CH.}}\ \underset{\displaystyle OH}{\underset{\displaystyle |}{CH_2}}$	8.76	130
$CH_3.\underset{\displaystyle OH}{\underset{\displaystyle |}{CH.}}\ \underset{\displaystyle OOH}{\underset{\displaystyle |}{CH_2}}$	14.80	130

1 ml. of potassium hydrogen phthalate solution (pH 4) and 4 ml. of 0.4M potassium iodide solution. The reaction was then followed by measurement of the absorption of tri-iodide ions.

The rate constant determined in this way was found to be 1.28×10^{-4} sec.$^{-1}$.

In order to measure the rate of reaction with iodide of the organic peroxide produced in the irradiated solutions, hydrogen peroxide was first removed by the use of the enzyme Catalase B (obtained from the Miles Chemical Co., New Jersey).

The rate constant for this reaction was found to be 1.36×10^{-4} sec.$^{-1}$ (Figures 24 and 25).

It can be seen that the rates of reaction for both the synthetic and radiolytic products are closely comparable. This provided perhaps not conclusive proof of but at least some strong evidence for the possible formation of the β-hydroxyethylhydroperoxide, and consequently gave an important clue to the probable nature of the organic peroxide detected in the irradiated solutions.

5. Effect of medium

(a) Irradiations in the presence of ferrous ions

Solutions of an ethylene-oxygen (20%) mixture under a total gas pressure of 25 atm. were

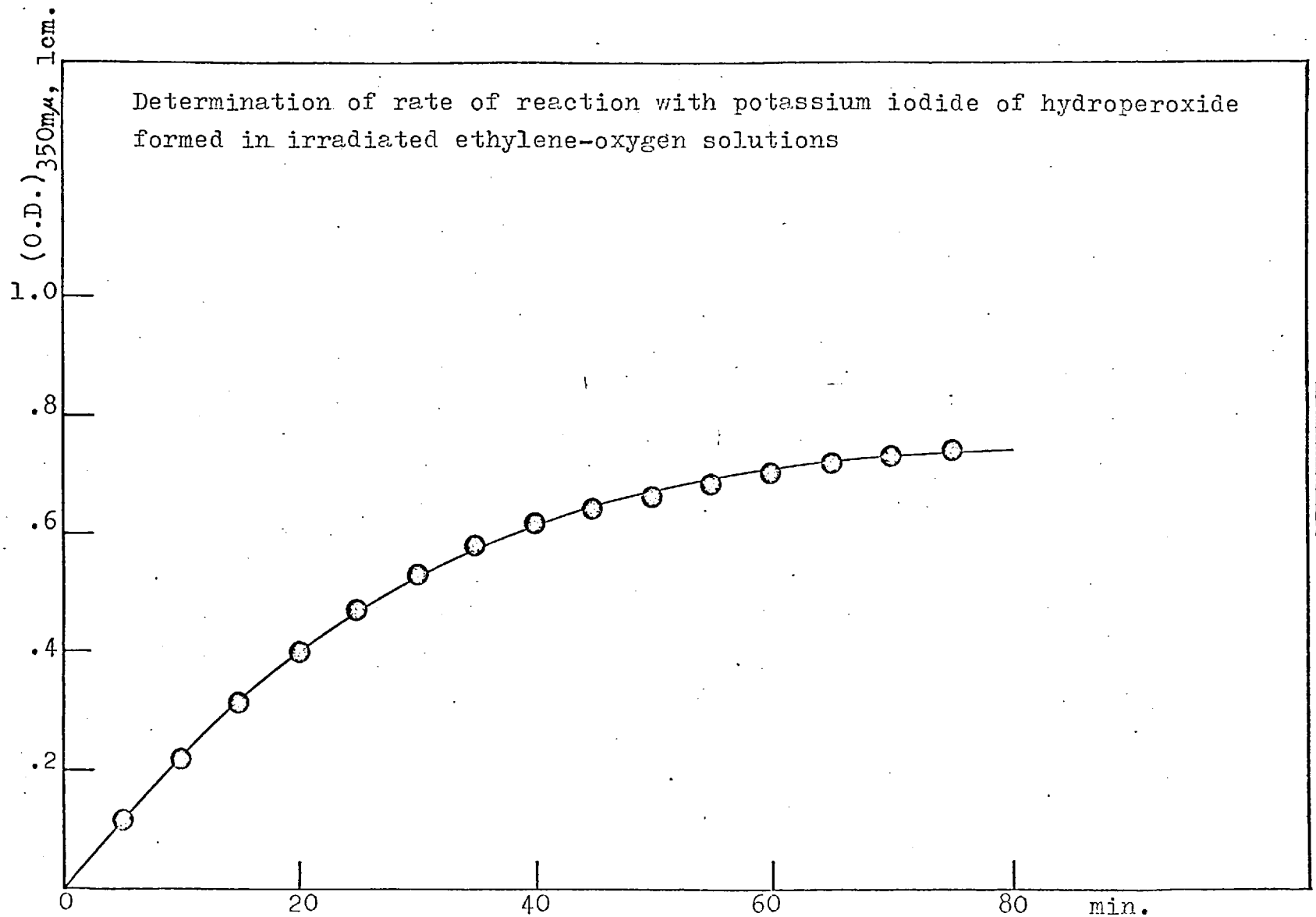

Determination of rate of reaction with potassium iodide of hydroperoxide formed in irradiated ethylene-oxygen solutions
(O.D.)350mμ, 1cm.
1.0
.8
.6
.4
.2
0
20
40
60
80
min.

Figure 24.

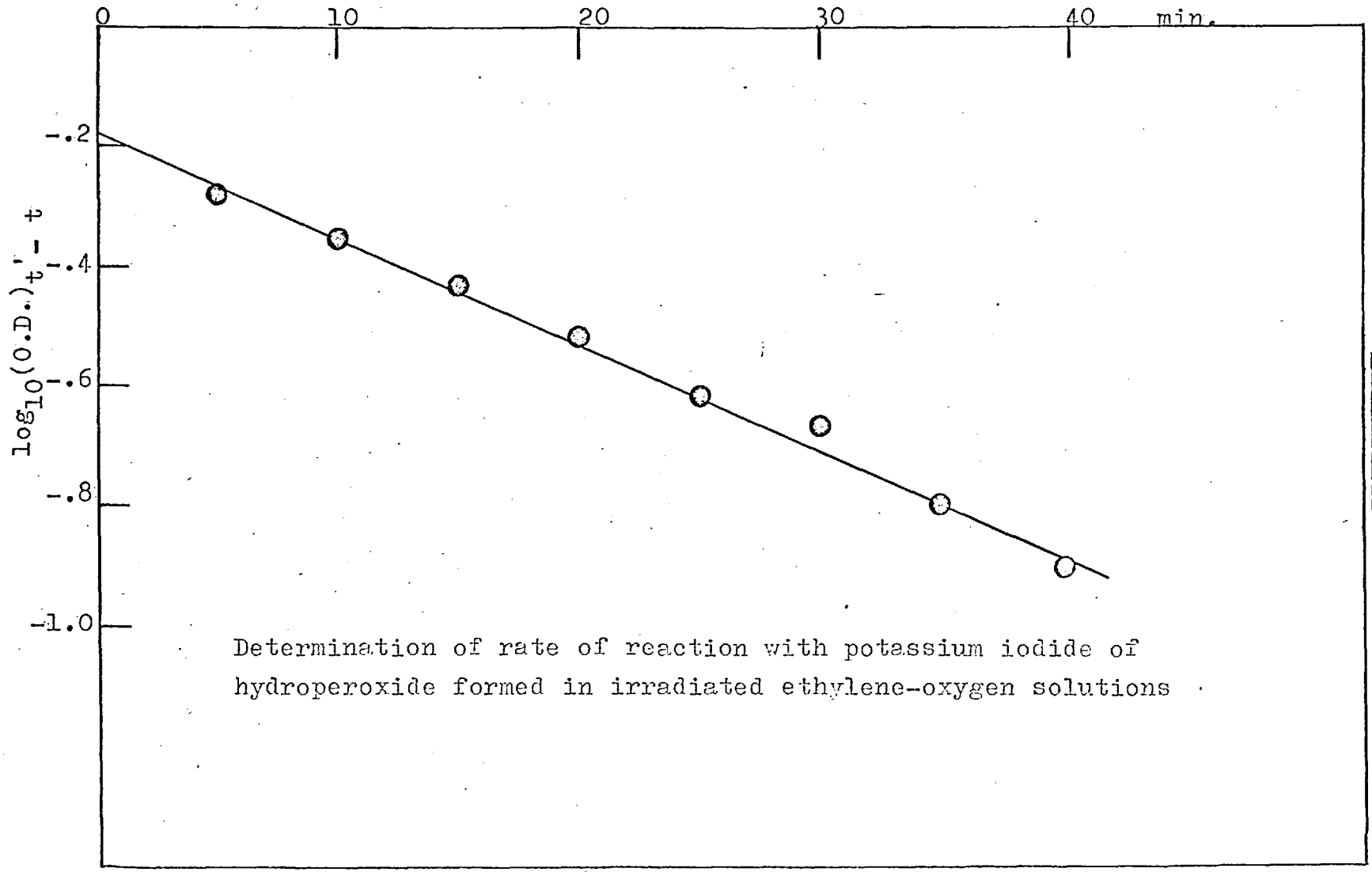


Figure 25.

Determination of rate of reaction with potassium iodide of hydroperoxide formed in irradiated ethylene-oxygen solutions

irradiated at a pH of 1.2 in the presence of ferrous ammonium sulphate.

Formaldehyde and acetaldehyde were both formed in high yield; the individual product yields are given in Table 17.

(b) Irradiations in the presence of hydrogen peroxide

Neutral solutions of the ethylent-oxygen (20%) mixture at 25 atm. were prepared in the presence of 10^{-3}M hydrogen peroxide, and irradiated over the dose-range 0 - 10^5 rads.

The aldehyde yield was as a result decreased, and there was at the same time a significant reduction in the yield of the organic hydroperoxide (Table 18). No hydrogen peroxide was formed during the radiolysis, and in fact, $G(-H_2O_2) = 0.10$ over the above dose-range.

C. Pulse radiolysis experiments

1. Introduction

The principle of the method has already been described (Section IIC). Kinetic data relating to the decay of transient species formed during a single pulse of radiation may be obtained from simultaneous photographs of the oscilloscope-screen at selected wavelengths. Measurements of this type have been made in the present work with ethylene in aqueous solution. Some typical results are shown in Plate 3.

TABLE 17

Irradiation of aqueous ethylene-oxygen (20%) solutions (25 atm., pH 1.2) in the presence of ferrous ions (dose-rate : 82,600 rads/hr.)

Dose-range : 0 - 20,700 rads

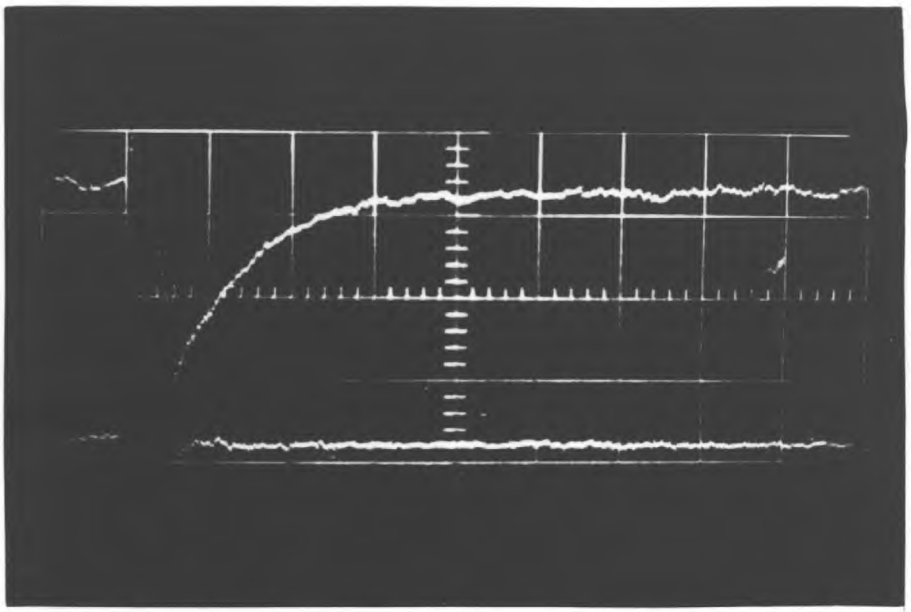
Product	Concentration of Fe^{2+}	
	10^{-3}M	10^{-2}M
G(HCHO)	5.70	6.19
G(CH_3CHO)	6.35	10.36
G(CH_3CH_2CHO)	0.93	2.08
G(Fe^{3+})	26.95	32.63

TABLE 18

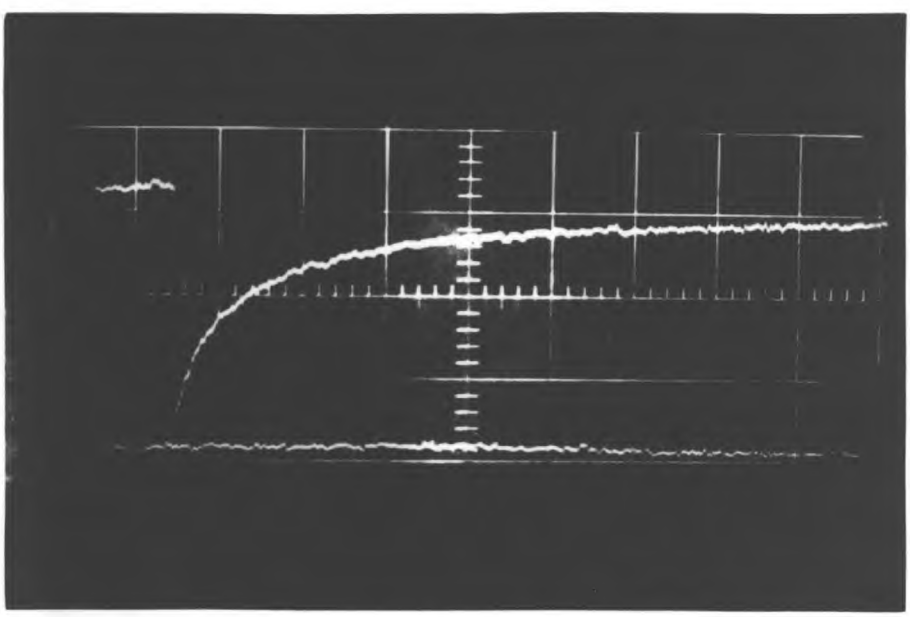
Irradiation of 10^{-3}M hydrogen peroxide solution containing ethylene-oxygen (20%) mixture under pressure (25 atm.); dose-rate, 82,600 rads/hr.

Product	G(molecules/100eV)
HCHO	0.25
CH_3CHO	1.23
CH_3CH_2CHO	0.14
ROOH	1.40

Plate 3.



(a) Ethylene solution at 510 millimicrons
Time-scale: 5 microseconds/cm.



(b) Ethylene-oxygen solution at 260 millimicrons
Time-scale: 100 microseconds/cm.

2. Ethylene solutions in the absence of oxygen

The photograph obtained for reaction of the solvated electron with ethylene in the irradiated solution is shown in Plate 3(a). Under the conditions of the experiment, the concentration of ethylene in the solution was ca. 5.4 x 10^{-3}M, so that this is effectively a pseudo-unimolecular reaction. Continued pulsing on the same sample of solution showed no change in the rate of reaction. At one stage, the sequence of irradiations was interrupted while ethylene was bubbled through the irradiation cell for a further 15 min. Again no change in the observed rate of reaction could be detected.

At a wavelength of 510 millimicrons and a dose per pulse of ca. 100 rads, the pseudo-unimolecular rate constant for the reaction of the solvated electron with an ethylene molecule was determined as 0.41 x 10^5 $sec.^{-1}$ at 20.8°C. The logarithmic plot of the optical density of the absorbing species against time after an electron pulse is shown in Figure 26. The corresponding bimolecular rate constant is 7.6 x 10^6 litre $mole^{-1}$ $sec.^{-1}$ (M^{-1} $sec.^{-1}$).

A very weak absorption band was detected in the irradiated solution over the range 275 - 400 millimicrons. The maximum absorption detected was about 0.2% at a wavelength of 350 millimicrons. The half-life of the absorbing species was estimated as ca. 1 msec, but no further

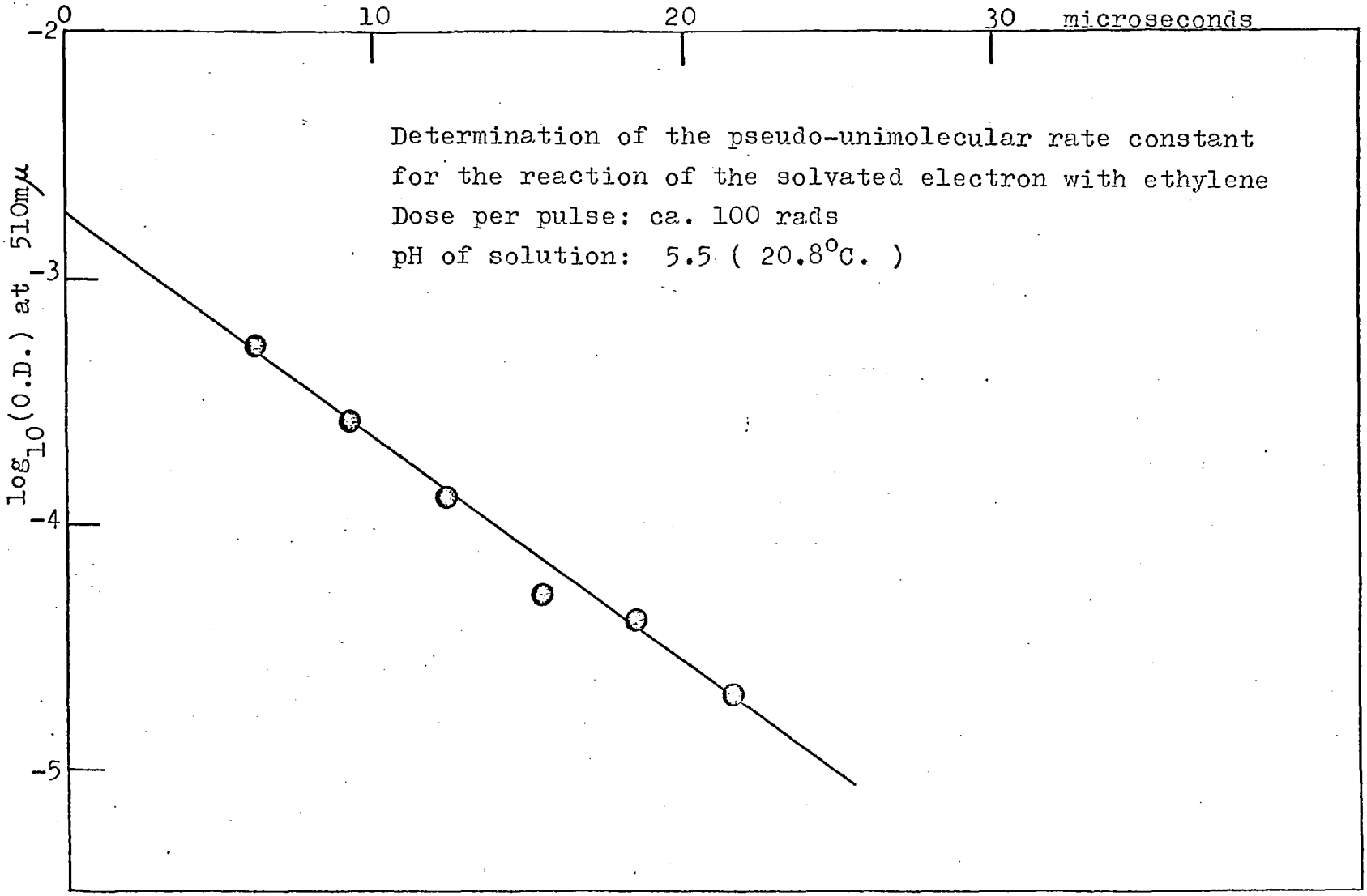

0
10
20
30
microseconds
-2
-3
-4
-5
log10(O.D.) at 510mμ
Determination of the pseudo-unimolecular rate constant
for the reaction of the solvated electron with ethylene
Dose per pulse: ca. 100 rads
pH of solution: 5.5 (20.8°C.)

Figure 26.

information was obtained.

2. Ethylene solutions in the presence of oxygen

At a wavelength of 510 millimicrons, the disappearance of solvated electrons by reaction with oxygen in the solution is so fast that no change in the absorption spectrum could be detected due to the reaction of the solvated electron with ethylene.

Examination of the absorption spectrum of the solution 50 microseconds after the electron pulse resulted in the detection of a strong absorption band in the region 230 - 300 millimicrons (Figure 27). Maximum absorption was measured at a wavelength of 260 millimicrons; the photograph of the decay of the absorbing species at this wavelength is shown in Plate 3(b). In these experiments the dose per pulse was ca. 5000 rads; continued pulsing of a sample of the ethylene-oxygen solution showed that the formation of the absorbing species at 260 millimicrons was strongly dependent on the concentration of oxygen in the solution.

Absorption at a wavelength of 250 millimicrons in oxygenated aqueous solutions irradiated with an electron beam has been tentatively assigned to the HO_2 radical[132]. However, the absorption observed in the present instance was not characteristic of that attributed to the above radical. It seems probable, therefore, that the absorption

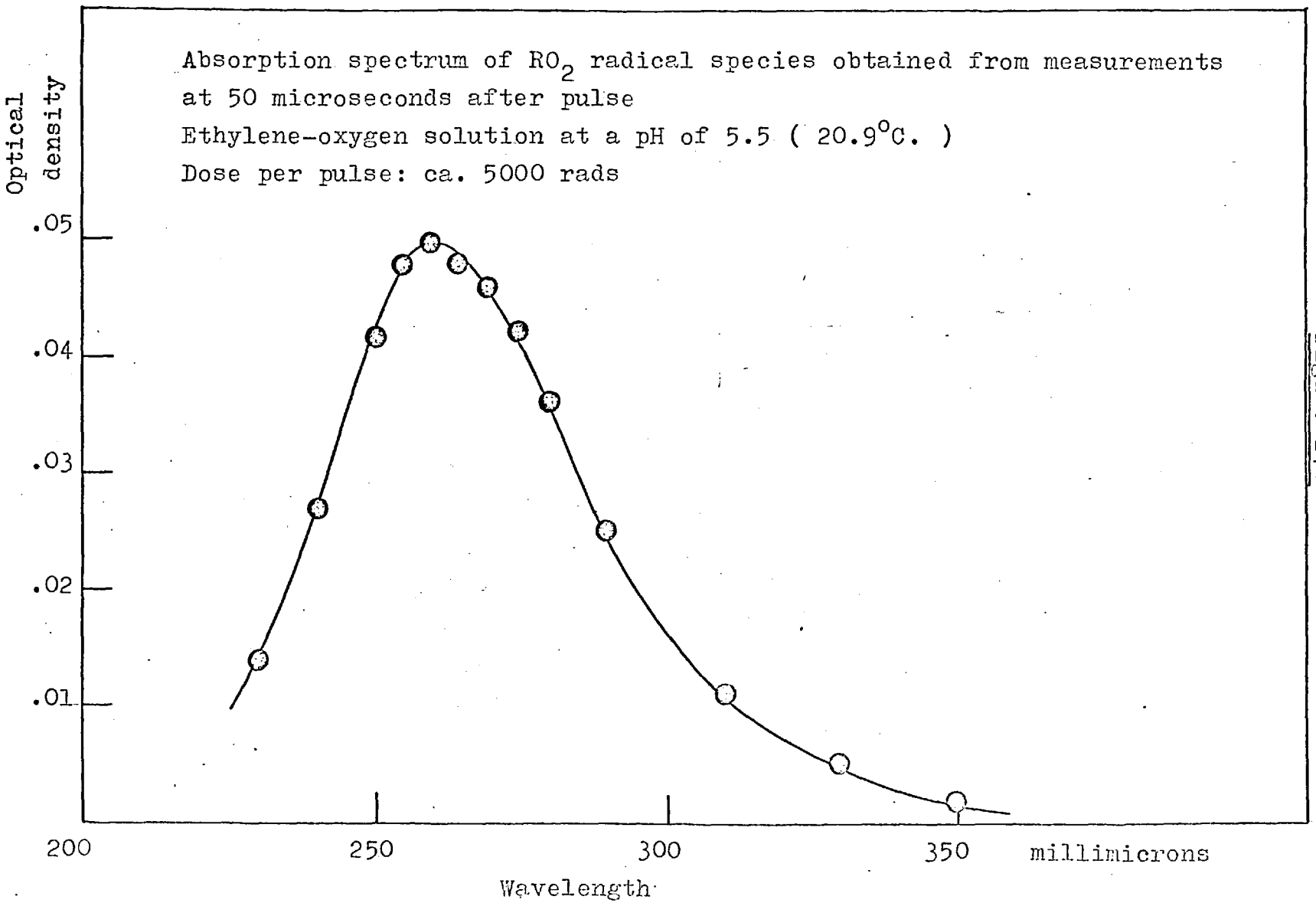

Absorption spectrum of RO_2 radical species obtained from measurements
at 50 microseconds after pulse
Ethylene-oxygen solution at a pH of 5.5 (20.9°C.)
Dose per pulse: ca. 5000 rads
Optical density
.05
.04
.03
.02
.01
200
250
300
350
millimicrons
Wavelength

Figure 27.

corresponds to an organic peroxy radical formed from ethylene. Since the solvated electron does not react readily with ethylene under these conditions, the identity of the peroxy radical may be consistent with the addition of hydroxyl radicals to ethylene, i.e., the species is probably $HOCH_2CH_2OO\cdot$.

Data relating to the decay of the peroxy radical at 260 millimicrons indicate that the disappearance follows a second-order kinetic law (Figure 28).

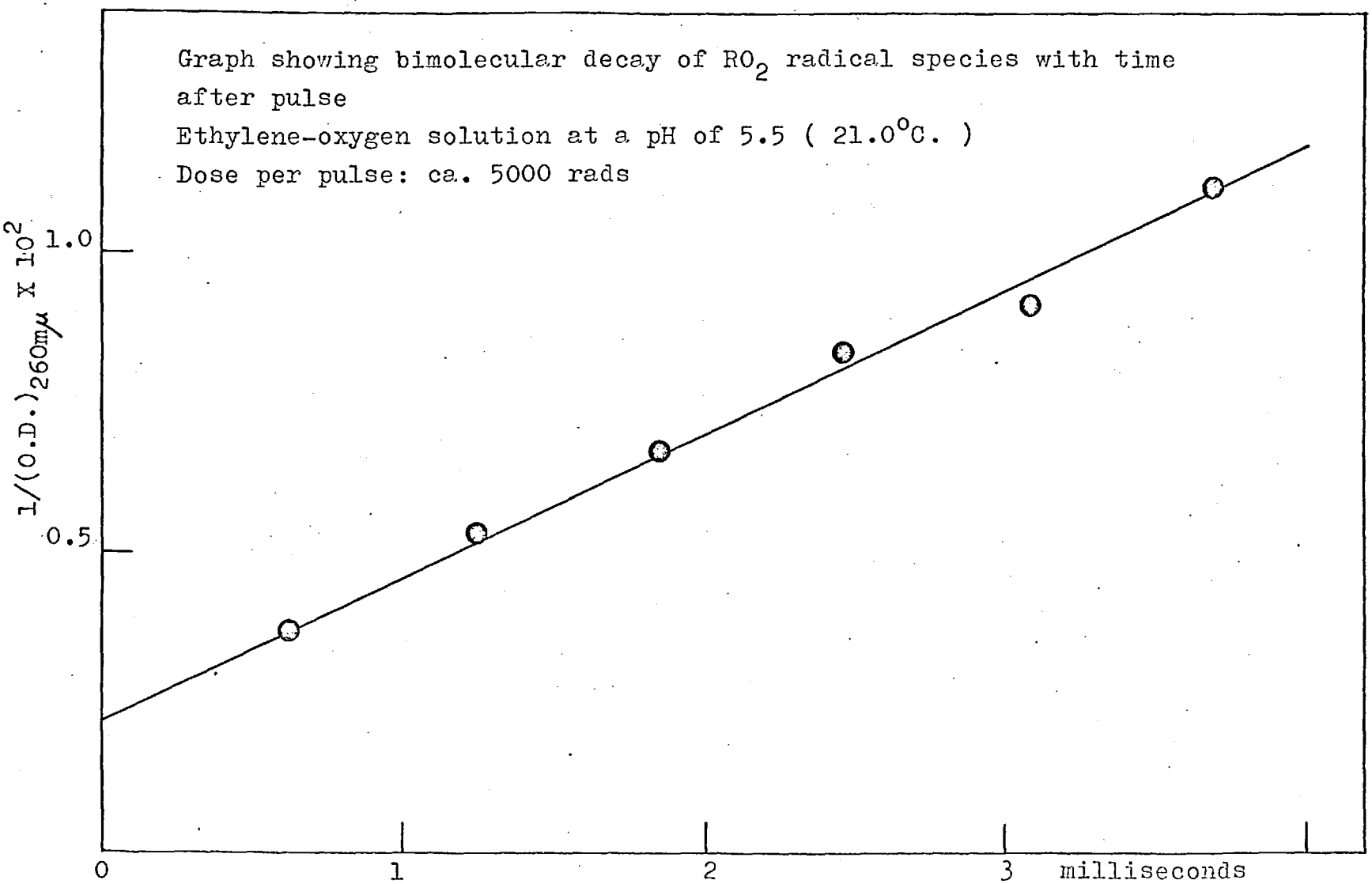

Graph showing bimolecular decay of RO_2 radical species with time after pulse
Ethylene-oxygen solution at a pH of 5.5 (21.0°C.)
Dose per pulse: ca. 5000 rads
$1/(O.D.)_{260m\mu} \times 10^2$
1.0
0.5
0
1
2
3
milliseconds

Figure 28.

SECTION IV

DISCUSSION

CONTENTS

		Page
A.	The initial effect of radiation	
1.	Introduction	194
2.	Neutral solution	197
3.	Acid solution	198
4.	Reactions involving oxygen	200
B.	Subsequent reactions in the absence of oxygen	
1.	Influence of ethylene concentration	202
2.	Reaction mechanism	
(a)	Neutral solution	203
(b)	Acid solution	205
(c)	Additives	207
(d)	Summary	210
C.	Subsequent reactions in the presence of oxygen	
1.	Introduction	211
2.	Reaction mechanism	
(a)	Neutral solution	211
(b)	Acid solution	213
(c)	Additives	217
(d)	Summary	219

A. The initial effect of radiation

1. Introduction

The primary aim in studies of the irradiation of organic compounds is to determine the chemical changes produced by the radiation. The secondary aim is then to elucidate the mechanism of formation of the various products. In dilute aqueous solution, the radiation is absorbed almost exclusively by the water. It is essential, therefore, in the present system to consider first the possible interactions of the different radical and ionic species present in irradiated water with the solute ethylene molecules.

Until recently (1960 - 62), it was generally accepted that the primary effect of radiation on water and aqueous solutions is to produce the species H and OH, together with hydrogen and hydrogen peroxide. However, from current work on the radiation chemistry of aqueous solutions[10,133], there is mounting evidence for the solvated electron, e^-_{aq}, as the precursor of the hydrogen atom.

Intense pulses of energetic electrons have been found to produce absorption in the visible region, which is attributed to the solvated electron. By following the decay of this absorption at 578 millimicrons, rate constants for a number of reactions of the solvated electron have been measured[134]. It has thus been shown that the solvated electron is stable enough to react with solutes such as

oxygen and hydrogen peroxide, and that the rate constants for the reactions concerned are not appreciably greater than those for other fast radical reactions, i.e., they are of the order of 10^{-11} molecule $^{-1}$ cm.^{3} sec.$^{-1}$.

The species formed by irradiation of water may thus be represented by the equation:

$$H_2O \longrightarrow H_2,\ H_2O_2,\ H^+_{aq},\ e^-_{aq},\ H,\ OH \qquad (1)$$

The rate constants for some of the possible reactions of the solvated electron with other species in equation (1) are given in Table 19. The solvated electron may also react with water in a first-order reaction:

$$e^-_{aq} \xrightarrow{H_2O} H + OH^- \qquad (2)$$

the rate constant for which is probably less than 10^4 sec.$^{-1}$ [10], although a more recent estimate[134] has set an upper limit on this quantity of 4×10^4 sec.$^{-1}$. With e^-_{aq} concentrations of from 2 to 30 micromolar in electron irradiations where the dose-rate is high, and second-order rate constant of about 10^{10} M^{-1} sec.$^{-1}$, it can be assumed that second-order reactions predominate. However, with gamma-rays, reaction (2) would be much faster than reaction (3) in neutral water:

$$e^-_{aq} + H^+_{aq} \longrightarrow H_{aq} \qquad (3)$$

The competition between reaction (2) and reaction (4),

$$e^-_{aq} + O_2 \longrightarrow O^-_{2aq} \qquad (4)$$

is not of course dependent on e^-_{aq} concentration.

As the acidity of the solution is increased, there is

TABLE 19

Rate constants for the reactions of the solvated electron at 21 - 23°C.[134]

Reaction	k (10^{10} M^{-1} $sec.^{-1}$)
$e^-_{aq} + H^+_{aq} \longrightarrow H_{aq}$	2.36 ± 0.24
$e^-_{aq} + H_2O_2 \longrightarrow OH^-_{aq} + OH$	1.23 ± 0.14
$e^-_{aq} + O_2 \longrightarrow O^-_{2aq}$	1.88 ± 0.20

a reduced probability of reaction between the solute and the solvated electron. In addition, below a pH value of ca.3, two additional entities, stoichiometrically equivalent to H and OH, are produced in equal yield, and these are probably H_2^+ and OH [135]. It has become necessary, therefore, to regard the conventional hydrogen atom yield as the composite quantity, $G_{'H'} = G_{e^-} + G_H + G_{H_2^+}$. The situation existing up to 10^{-8} sec. in the track of a fast charged particle of low LET is thus represented by the equation:

$$G_{-H_2O}H_2O \longrightarrow G_{'H'}'H' + G_{OH}OH + G_{H_2}H_2 + G_{H_2O_2}H_2O_2 \quad (5)$$

where the coefficients G_{-H_2O}, $G_{'H'}$, etc. refer to the respective 'radical' and 'molecular' yields produced per 100eV of radiation energy absorbed by the water. In addition, these coefficients represent the numbers of radicals which are available to react with solutes per 100eV of absorbed energy.

2. Neutral solution

From the pulse radiolysis studies carried out in the present work with neutral solutions of ethylene in the absence of oxygen, the rate constant for the reaction of the solvated electron with ethylene has been determined as $7.6 \times 10^6 M^{-1}$ sec.$^{-1}$. This value compares favourably with that of 10^6-$10^7 M^{-1}$sec.$^{-1}$ reported by Hart [136]. Thus, despite the high intrinsic reactivities of e^-_{aq} with the other species in irradiated water, the conditions in neutral solution are very favourable for its comparatively fast reaction with

ethylene.

$$e^-_{aq} + C_2H_4 \longrightarrow C_2H_4^- \qquad (6)$$

The ionic species formed in reaction (6) might be expected to react further, for example, according to the equations:

$$C_2H_4^- + H_2O \longrightarrow C_2H_5 + OH^- \qquad (7)$$

or $$C_2H_4^- + H^+ \longrightarrow C_2H_5 \qquad (8)$$

The overall reaction would thus correspond to the addition of a hydrogen atom to an ethylene molecule. However, in the absence of oxygen both the ionic species, $C_2H_4^-$, and the ethyl radical may serve to initiate polymerisation:

$$C_2H_4^- + nC_2H_4 \longrightarrow \left[-CH_2CH_2-\right]_{n+1} + e^- \qquad (9)$$

or $$C_2H_5 + nC_2H_4 \longrightarrow CH_3\left[-CH_2-\right]_{2n+1} \qquad (10)$$

3. Acid solution

In acid solution, the principal reducing species are hydrogen atoms formed according to reaction (3). Both hydrogen atoms and hydroxyl radicals will abstract hydrogen from saturated hydrocarbons, although little is known about the subsequent fate of the resulting alkyl radicals in an aqueous medium. With unsaturated hydrocarbons, such as ethylene, the hydrogen atom and hydroxyl radical may add to the double bond rather than abstract hydrogen. Addition of free radicals to olefins is plausible on energetic grounds, and is substantiated by work on thermal oxidation[137].

The reaction of hydrogen atoms with ethylene has been studied in connection with the photosensitised hydrogenation

of this olefin in the gas phase. Although both hydrogenation and dehydrogenation can probably occur, i.e.,

$$H + C_2H_4 \longrightarrow C_2H_5 \qquad (11)$$

$$H + C_2H_4 \longrightarrow C_2H_3 + H_2 \qquad (12)$$

the available evidence points to reaction (11) being fast, with an activation energy ca. 5 kcal.mole^{-1} [138]. More recent determinations[139,140] give the activation energy of the addition reaction as 4.1 and 3.7 kcal.mole^{-1} respectively; the rate constant for reaction (11) at 18°C. is given as 7.5×10^{11} mole^{-1} cm.^{3} sec.$^{-1}$ [140]. There is less definite evidence for the occurrence of reaction (12), and in any case, the activation energy requirements for transfer appear to be more stringent[141].

There is on the other hand no comparable information available regarding the kinetic parameters for the straightforward addition of hydroxyl radicals to ethylene:

$$OH + C_2H_4 \longrightarrow C_2H_4OH \qquad (13)$$

Transfer reactions of hydroxyl radicals with saturated hydrocarbons,

$$OH + RH \longrightarrow H_2O + R \qquad (14)$$

are however exothermic to the extent of 20 kcal.mole^{-1}, and might, therefore, be expected to have low activation energies. Earlier studies[142] of these reactions in the gas phase suggested that the activation energies are as high as 7 - 10 kcal.mole^{-1}, but more recent results[143] have indicated values for the reactions of hydroxyl radicals with simple alkanes in

aqueous solution of only 1 - 2 kcal.mole^{-1}. Henley et al.[79] suggested a transfer reaction as the initiation step in the radiation-induced oxidation of ethylene in aqueous solution:

$$OH + C_2H_4 \longrightarrow \dot{C}HCH_2 + H_2O \qquad (15)$$

but there is little evidence[141] in support of this type of reaction with unsaturated hydrocarbons, and such processes may probably by largely discounted in comparison with addition.

In radiation-chemical systems, the reactions of the hydroxyl radical are less variable than those of the solvated electron and the hydrogen atom, since in its unionised form, this radical probably reacts at the same rate in acid and neutral solutions. Few absolute rate constants are available for its reactions, but those recorded at ambient temperatures include $k_{OH + H_2O_2} = 4.5 \times 10^7 M^{-1} sec.^{-1}$ and $k_{OH + OH} = 4.9 \times 10^9 M^{-1}$ sec.$^{-1}$ [144].

At a pH of 1.2, the initial reactions of hydrogen atoms and hydroxyl radicals therefore involve predominantly addition to the ethylene double bond:

$$H + CH_2 = CH_2 \longrightarrow CH_3CH_2 \qquad (11)$$

$$OH + CH_2 = CH_2 \longrightarrow CH_2CH_2OH \qquad (13)$$

4. Reactions involving oxygen

In the presence of oxygen, the solvated electron reacts solely with oxygen (compare Section IIIC):

$$e^-_{aq} + O_2 \longrightarrow O_2^-{}_{aq} \qquad (16)$$

The O_2^- ion formed in the reaction may equilibrate with

hydrogen ions present in the solution:

$$HO_2 \rightleftharpoons H^+ + O_2^- \qquad (17)$$

Alternatively, it may exist as a reactive species in the medium. The HO_2 radical is however believed to be an acid with a pK value of ca. 2 [145], and would therefore be ca. 50% dissociated at a pH of 2. In neutral solutions of ethylene (pH 5.5), the reactive entity must be the O_2^- ion. The disappearance of an alkyl peroxy radical during pulse radiolysis of ethylene-oxygen solutions has already been described (Section IIIC). Since the addition of hydroxyl radicals to ethylene appears to take place fairly rapidly, the most probable peroxy radical to be formed in the solutions is the β-hydroxyethylhydroperoxy radical:

$$OH + CH_2{=}CH_2 \longrightarrow HOCH_2CH_2 \qquad (13)$$

$$HOCH_2CH_2 + O_2 \longrightarrow HOCH_2CH_2O_2 \qquad (18)$$

In acid solution, the O_2^- ion exists almost exclusively as the perhydroxyl radical, HO_2 . In fact at a pH of 0, the ratio O_2^- : HO_2 is approximately 1:100. Under these conditions, and at the solute concentrations attained in the present study, the HO_2 radical may therefore also undergo addition reactions with ethylene:

$$HO_2 + C_2H_4 \longrightarrow HO_2CH_2CH_2 \qquad (19)$$

Since the solvated electron reacts extremely rapidly with hydrogen ions, the perhydroxyl radical may also be formed by direct addition of hydrogen atoms to molecular oxygen:

$$H + O_2 \longrightarrow HO_2 \qquad (20)$$

the rate constant for which at ambient temperatures is quoted as $k_{H+O_2} = 1.2 \times 10^{10}\ M^{-1}\ sec.^{-1}$ [146].

In acid solutions, and in the presence of oxygen, most of the observed oxidation products in the present system, therefore, probably result from the initial addition to ethylene of OH and HO_2 radicals.

B. Subsequent reactions of ethylene in the absence of oxygen

1. Influence of ethylene concentration

One of the experimental difficulties associated with the study of the radiation-induced reactions of ethylene is its relatively low solubility in water (Table 2). The solute concentration can be an important factor in the radiation chemistry of aqueous solutions[147]. It follows from the radical diffusion model that the total yield of water decomposition should be nearly independent of solute concentration, whereas the yield of molecular products should diminish slowly as the concentration of scavenging solutes is increased. On this basis, the chemical yield should be independent of solute concentration over a fairly wide range, provided that sufficient solute is present to utilise all the available radicals produced from the solvent. For dilute aqueous solutions, it has usually been supposed that this in fact always holds. With organic solutes, however,

no clear experimental evidence has been presented in support of such a generalisation. In most of the cases so far investigated, the yield does not become independent of the solute concentration below 1M.

In the present system, the irradiation of solutions containing from 0.027 to 0.200M ethylene yields polyethylene as the principal product as well as acetaldehyde, n-butyraldehyde, higher molecular weight aldehydes, and hydrogen peroxide. Under the conditions used, the measured polymer yields increase with ethylene concentration (Figure 5), whereas the yields of aldehyde and peroxide are independent of ethylene concentration (Table 7).

2. Reaction mechanism

(a) Neutral solution

In neutral solution, the solvated electron undergoes a relatively fast reaction with ethylene ($k^{20.8°C.} = 7.6 \times 10^6\ M^{-1}\ sec.^{-1}$). The reaction of the solvated electron with hydrogen ions is also a fast reaction ($k^{21°C.} = 2.4 \times 10^{10}\ M^{-1}\ sec.^{-1}$)[134]. In the irradiation of aqueous ethylene solutions, the condition for the two rates of reaction being equal is:

$$k\ [e][C_2H_4] = k'[e][H^+]$$

$$[H^+] = \frac{k}{k'}[C_2H_4] \qquad (21)$$

With an ethylene pressure of 20 atm. above the solution, the

condition represented by equation (21) corresponds to a pH of ca. 4 in the solution. At a pH of 1.2, the increased polymer yield over the value obtained at a pH of 5.5 (Figure 10) can be attributed, therefore, to more efficient initiation of polymerisation by hydrogen atoms than by $C_2H_4^-$ ions.

The radical $\dot{C}H_2CH_2OH$, formed in both neutral and acid solution, may also serve to initiate polymerisation by successive reaction with monomeric ethylene. However, no evidence of oxygen-containing groups was obtained on infra-red examination of the polymer samples, which at least indicates that long chains are set up during the reaction. This observation has recently been confirmed in a study of the radiation-induced polymerisation of olefins in aqueous solutions of silver salts[148]. The silver ions apparently act as electron transfer agents, the radicals subsequently formed initiating the reaction chain. The ethylene solutions yielded solid polymers of high molecular weight. With a dose-rate of 7×10^3 rads/hr. and an ethylene concentration of ca. 0.04M, the polymer yield corresponded to a G-value of 0.6×10^5. In contrast, in the present study, $G(-C_2H_4) = 95.5$ at an ethylene concentration of 0.2M and a dose-rate of 9×10^4 rads/hr.

Termination of the chain polymerisation may involve disproportionation or recombination of the participating radicals, e.g.,

$$2\ (CH_2)_nOH \longrightarrow CH_3(CH_2)_{n-2}CHO + CH_3(CH_2)_{n-1}OH \quad (22)$$

$$2\ (CH_2)_nOH \longrightarrow (CH_2)_{2n}(OH)_2 \quad (23)$$

These types of reaction probably account for the small amount of long-chain aldehydes reported at comparatively low total doses (Section IIIA).

At a pH of 5.5, other oxidation products, such as acetaldehyde, may arise from disproportionation of $\dot{C}H_2CH_2OH$ radicals:

$$2\ CH_2CH_2OH \longrightarrow CH_3CHO + CH_3CH_2OH \quad (24)$$

although the low yields of the above aldehyde ($G(CH_3CHO) = 0.23$) indicate that this is not an important process. A similar reaction has been suggested however for the interaction of isomeric ethoxy radicals, C_2H_5O, in the gas phase[149]. The presence of an alcohol in the irradiated solutions was not confirmed, but the sensitivity of the method used was not comparable with that employed for the determination of aldehydes.

(b) Acid solution

In 0.1N sulphuric acid, the following equation would account for the decomposition of water by gamma-rays:

$$4.45\ H_2O \longrightarrow 3.65H + 2.85OH + 0.4H_2 + 0.8H_2O_2 \quad (25)$$

The numbers in this equation are the G-values given by Johnson and Weiss[150]. At a pH of 1.2, G(total aldehyde) = 0.55, and $G(H_2O_2) = 0.42$. These values may be compared with those

obtained by Weiss et al.[80] at the same pH but at a solute concentration of 0.004M, viz., G(total aldehyde) = 0.24 and $G(H_2O_2)$ = 0.40. These results suggest that about one-half of the 'molecular' hydrogen peroxide yield may have been used up in aldehyde formation. This type of reaction is particularly prominent during the decomposition of formic acid[42]:

$$COOH + H_2O_2 \longrightarrow CO_2 + H_2O + OH \qquad (26)$$

However, the free radicals formed in ethylene radiolysis do not react readily with hydrogen peroxide (Section IIIA). Under the widely different concentration conditions of ethylene and hydrogen peroxide in the irradiated solutions, any molecular hydrogen peroxide formed is probably 'protected' from free radical attack by the reactive ethylene. Since $G(H_2O_2)$ + G(acetaldehyde) = 0.81 at a pH of 1.2, and $G_{H_2O_2}$ = 0.80, the acetaldehyde may be formed by a radiation-induced reaction between an alcohol and hydrogen peroxide[151]:

$$RCH_2OH + H_2O_2 \longrightarrow RCHO + 2H_2O \qquad (27)$$

In addition, oxidative termination of the polymerisation may result in the production of higher aldehydes, such as n-butyraldehyde:

$$HOCH_2CH_2 + CH_2 = CH_2 \longrightarrow HOCH_2CH_2CH_2CH_2 \qquad (28)$$

The radicals formed in reaction (28) may then undergo oxidation rather than react with monomeric ethylene:

$$HOCH_2CH_2CH_2CH_2 \longrightarrow \left[HOCH_2CH_2CH_2CH_2\right]^+ \qquad (29)$$

$$\left[HOCH_2CH_2CH_2CH_2\right]^+ \longrightarrow CH_3(CH_2)_2CHO + H^+ \qquad (30)$$

(c) Additives

Experiments carried out in the presence of ferric ions at a pH of 1.2 have shown an acceleration of the oxidation step at the expense of polymerisation. Under these conditions, the ferric ions are simultaneously reduced so that this becomes an example of coupled oxidation-reduction. The organic free radicals produced from ethylene must act as reducing agents so that the increased acetaldehyde yields may be accounted for in the following way:

$$HOCH_2CH_2 + Fe^{3+} \longrightarrow \left[HOCH_2CH_2\right]^+ + Fe^{2+} \quad (31)$$

$$\left[HOCH_2CH_2\right]^+ \longrightarrow CH_3CHO + H^+ \quad (32)$$

In the presence of 10^{-2}M ferric ions, $G(CH_3CHO) = 1.07$. However, $G(Fe^{2+}) = 5.50$ so that the above reaction sequence must include the further reduction step:

$$H + Fe^{3+} \longrightarrow H^+ + Fe^{2+} \quad (33)$$

Since $G_H + G_{OH} = 6.50$, some radicals are evidently still effective in initiating polymerisation; the extent of such polymerisation was however too small to allow estimation in these solutions. Hydrogen peroxide reacts with ferrous ions according to the equation:

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + OH^- + OH \quad (34)$$

The hydroxyl radical produced will react with ethylene, followed by reaction (31), so that reaction (34) does not influence the overall reaction. The yield of ferrous ions

should thus correspond to $G(Fe^{2+}) = 6.50$ (cf., measured value $G(Fe^{2+}) = 5.50$). At the ethylene concentrations used in these experiments (0.1M), hydroxyl radicals are obviously more effective in initiating polymer chains than in increasing the oxidation yield according to reactions (31) and (32).

The experiments carried out in neutral solution and in the presence of 10^{-3}M hydrogen peroxide (Section IIIA) have indicated clearly that the following reaction predominates:

$$e^-_{aq} + H_2O_2 \longrightarrow OH^- + OH \qquad (35)$$

Reaction (35) has been shown[134] to be considerably faster than the competing process[144]:

$$OH + H_2O_2 \longrightarrow HO_2 + H_2O \qquad (36)$$

Nevertheless, polymerisation does take place indicating that hydroxyl radicals may also be effective in initiating reaction chains. The perhydroxyl radicals formed according to reaction (36) also add to ethylene:

$$HO_2 + CH_2 = CH_2 \longrightarrow HO_2CH_2CH_2 \qquad (19)$$

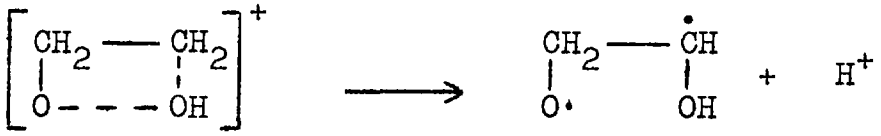
The resulting radical may, by the sequence of reactions outlined below, lead to the formation of the substantial amounts of formaldehyde ($G(HCHO) = 1.99$), which are found in the presence of hydrogen peroxide.

$$H + H_2O_2 \longrightarrow H_2^+ + HO_2^- \qquad (37)$$

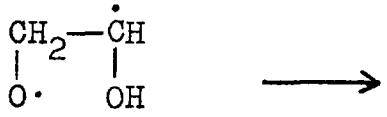
$$H_2^+ + \underset{\underset{OOH}{|}}{CH_2CH_2} \longrightarrow \underset{\underset{OOH}{|}}{CH_2\overset{+}{C}H_2} + H_2 \qquad (38)$$



(39)

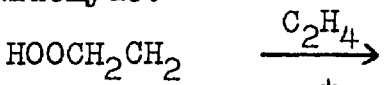


(40)

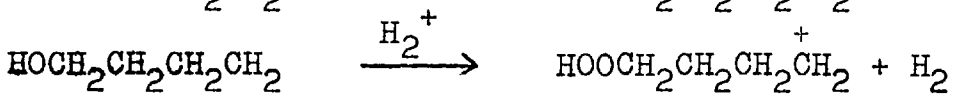


(41)

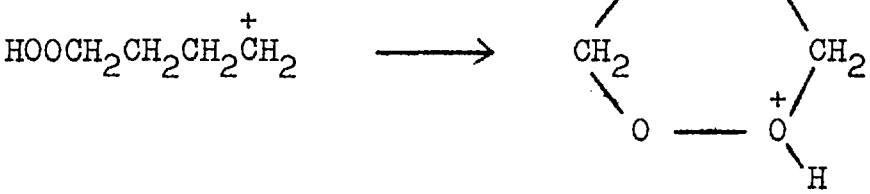
A similar mechanism could also account for the formation of propionaldehyde:



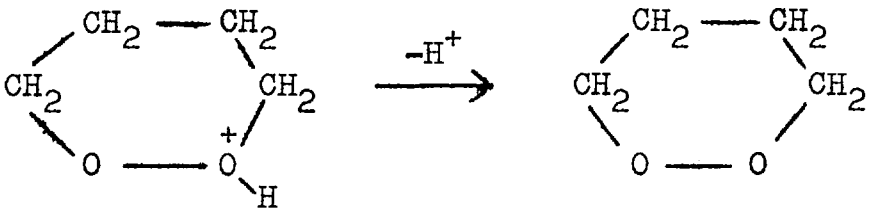
(42)



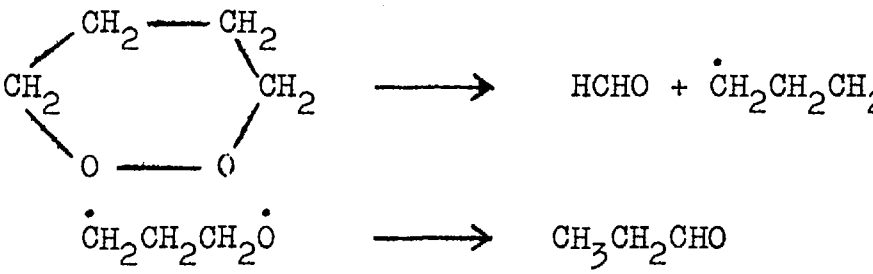
(43)



(44)



(45)



(46)

(47)

(d) Summary

The more important reactions of ethylene which are believed to take place in the in the absence of oxygen may thus be summarised:

(i) in neutral solution,

$$e^-_{aq} + C_2H_4 \longrightarrow C_2H_4^-$$

$$C_2H_4^- + H_2O \longrightarrow C_2H_5 + OH^-$$

$$C_2H_4^- + H^+ \longrightarrow C_2H_5$$

$$OH + C_2H_4 \longrightarrow HOCH_2CH_2$$

$$\left.\begin{matrix} C_2H_4^- \\ C_2H_5 \\ HOCH_2CH_2 \end{matrix}\right) \xrightarrow{C_2H_4} \text{polymer}$$

$$HOCH_2CH_2 \xrightarrow{\text{oxidation}} \left[HOCH_2CH_2\right]^+ \longrightarrow CH_3CHO + H^+$$

(ii) in acid solution,

$$H + C_2H_4 \longrightarrow C_2H_5$$

$$OH + C_2H_4 \longrightarrow HOCH_2CH_2$$

$$\left.\begin{matrix} C_2H_5 \\ HOCH_2CH_2 \end{matrix}\right) \xrightarrow{C_2H_4} \text{polymer}$$

$$HOCH_2CH_2 \xrightarrow{\text{oxidation}} \left[HOCH_2CH_2\right]^+ \longrightarrow CH_3CHO + H^+$$

C. Subsequent reactions in the presence of oxygen

1. Introduction

The presence of oxygen in the irradiated solution markedly alters the course of the reaction. Polymerisation of ethylene is immediately inhibited. This effect has already been confirmed in the radiation-induced gas phase polymerisation of ethylene, and it has been shown that the oxidation product does not catalyse the reaction[152].

2. Reaction mechanism

(a) Neutral solution

The fast reaction of solvated electrons with solute oxygen molecules in neutral solution has already been discussed. This precludes any direct reaction between electrons and ethylene. Hydroxyl radicals will however add to ethylene to form the $HOCH_2\dot{C}H_2$ radical, which then reacts with oxygen to yield eventually the various oxidation products found. The RO_2 radical detected during the pulse radiolysis experiments (Section IIIC) is almost certainly the β-hydroxyethylhydroperoxy radical, which decays bimolecularly by processes such as:

$$2\ HOCH_2CH_2O_2 \longrightarrow 2HOCH_2CH_2O\cdot + O_2 \qquad (48)$$

$$HOCH_2CH_2O\cdot \longrightarrow HO\dot{C}H_2 + HCHO \qquad (49)$$

$$HOCH_2CH_2O\cdot + HOCH_2CH_2O_2 \longrightarrow CH_2OH.CHO + HOCH_2CH_2O_2H \qquad (50)$$

The O_2^- ion may also be involved in reactions with the $HOCH_2\dot{C}H_2$ radical:

$$HOCH_2CH_2 + O_2^- \longrightarrow \left[HOCH_2CH_2O_2\right]^- \quad (51)$$

$$\left[HOCH_2CH_2O_2\right]^- + H_2O \longrightarrow HOCH_2CH_2O_2H + OH^- \quad (52)$$

The high yields of stable organic hydroperoxide, G(ROOH) = ca. 4 (Table 14), suggest that reactions (51) and (52) are important. The reaction of O_2^- ions with RO_2 radicals:

$$HOCH_2CH_2O_2 + O_2^- \longrightarrow \left[HOCH_2CH_2O_2\right]^- + O_2 \quad (53)$$

may also supplement reactions (51) and (52).

Direct addition of O_2^- ions to ethylene could account for the aldehydic products:

$$O_2^- + CH_2 = CH_2 \longrightarrow \left[CH_2CH_2O_2\right]^- \quad (54)$$

$$\left[CH_2CH_2O_2\right]^- + H^+ \longrightarrow CH_3CH_2O_2 \quad (55)$$

$$CH_3CH_2O_2 + O_2^- \longrightarrow CH_3CHO + O_2 + OH^- \quad (56)$$

The relative importance of the reactions suggested cannot be assessed without a knowledge of the individual rate constants. The experimental evidence indicates that several of the reactions are probably strongly dependent on the oxygen concentration.

At a pH of 5.5, and according to the equilibrium:

$$HO_2 \rightleftharpoons H^+ + O_2^-$$

the steady state concentration of HO_2 radicals will be extremely small. Hydrogen peroxide formation by the

combination reaction:

$$2HO_2 \longrightarrow H_2O_2 + O_2 \qquad (57)$$

is thus limited. The closeness of the observed yield of hydrogen peroxide (Table 14) to the molecular yield bears this out, and eliminates the possible formation of hydrogen peroxide by an alternative mechanism.

(b) Acid solution

In acid solution, molecular oxygen will tend to add to the ethyl radicals formed from ethylene:

$$CH_3CH_2 + O_2 \longrightarrow CH_3CH_2O_2 \qquad (58)$$

The resulting ethylperoxy radicals are a probable source of the acetaldehyde formed. Although the breakdown of such radicals in the gas phase takes place almost exclusively at surfaces[153,154]:

$$CH_3CH_2O_2 \xrightarrow{\text{wall}} CH_3CHO + OH \qquad (59)$$

other mechanisms probably will operate in solution. Other oxidation products formed in acid solution may result from primary attack on ethylene by hydroxyl and perhydroxyl radicals:

$$OH + CH_2 = CH_2 \longrightarrow HOCH_2CH_2 \qquad (13)$$

$$HO_2 + CH_2 = CH_2 \longrightarrow HO_2CH_2CH_2 \qquad (19)$$

and both of the resulting radicals may react further with oxygen in the solution:

$$HOCH_2CH_2 + O_2 \longrightarrow HOCH_2CH_2O_2 \qquad (18)$$

$$HO_2CH_2CH_2 + O_2 \longrightarrow HO_2CH_2CH_2O_2 \qquad (60)$$

Little is known about the formation of aldehydes from these peroxy radicals, although many of the observed products in this instance must arise from mutual oxidation-reduction reactions between the various species.

Weiss et al.[80] have reported the yields G(HCHO + CH_3CHO) = 3.0, G($CH_2OH.CHO$) = 2.5, G(H_2O_2) = 2.6 and G(ROOH) = 0.4 in solutions containing 3 x 10^{-3}M ethylene and 3 x 10^{-4}M oxygen. At concentrations between 10^{-4} and 10^{-2}M ethylene, the system showed little dependence of yields on concentration.

In the present study, at an ethylene concentration of 0.1M, and increase in the relative amount of oxygen from 10 to 40% in the gas mixture reduces the yield of acetaldehyde (Figure 21). The corresponding yields of hydrogen peroxide and organic hydroperoxide, however, are independent of oxygen concentration over this range (Figure 23). It seems probable that at the lower oxygen concentrations, the reaction

$$H + C_2H_2 \longrightarrow CH_3CH_2 \xrightarrow{O_2} CH_3CH_2O_2$$

is favoured in comparison with the reaction

$$H + O_2 \longrightarrow HO_2$$

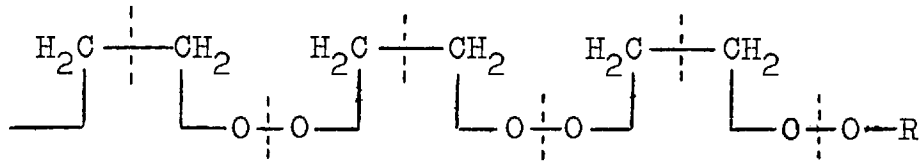
In this concentration region, i.e., below 10% oxygen in the gas mixture, there may be additional competition between the reactions already enumerated on the one hand, and polymerisation on the other. The evidence relating to the

formation of long-chain aldehydes at low oxygen concentrations (Section IIIB) conforms with this suggestion. The favoured addition of radicals to ethylene is particularly relevant to the present results in view of the high pressures of ethylene equilibrated with the solutions.

A possible mechanism which could explain some of the experimental results is suggested by analogy with liquid phase oxidation studies of olefins[68,155]. This would involve co-polymerisation of ethylene and oxygen followed by breakdown of the co-polymer chain. Thus, after initial production of peroxy radicals, RO_2, in the system, addition of these radicals to ethylene might take place:

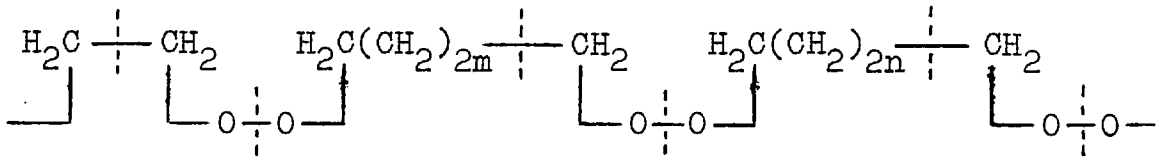
$$CH_2 = CH_2 + RO_2 \longrightarrow CH_2—CH_2\text{—}O—O—R \qquad (61)$$

This reaction could be followed by further alternate addition of oxygen and ethylene leading eventually to chains such as:



Breakdown of this copolymer by fission of the O - O and C - C bonds shown would then yield formaldehyde as well as smaller amounts of acetaldehyde, which could result from rearrangements of the end-groups. In the presence of only small quantities of oxygen, copolymer chains containing less oxygen than ethylene and with perhaps a random arragement of ethylene

molecules will tend to be formed:



The decomposition products from this type of asymmetric co-polymer chain could conceivably include aldehydes with an odd number of carbon atoms, such as propionaldehyde, or even higher primary aliphatic aldehydes.

Hydrogen peroxide is formed in the ethylene-oxygen solutions at a pH of 1.2, and the yield has been determined as a function of oxygen concentration (Figure 23). The initial yields of hydrogen peroxide, in contrast to those of the aldehydic products, are independent of oxygen concentration over the range investigated (0 - 0.02M). At a fixed oxygen concentration in the solution, the yield of hydrogen peroxide usually becomes independent of the organic solute concentration when the latter exceeds about 10^{-3}M [147].

The comparatively high yield, G(ROOH) = ca. 3, of stable organic hydroperoxide formed in acid solutions is a somewhat unusual feature of the results obtained in this system. This product again shows almost complete independence on oxygen concentration. It has already been proposed (Section IIIB) that β-hydroxyethylhydroperoxide is the product formed. The most likely mechanism is one involving the interaction of the $HOCH_2CH_2OO\cdot$ radical with some hydrogen donor:

$$HOCH_2CH_2O_2 + XH \longrightarrow HOCH_2CH_2O_2H + X \qquad (62)$$

According to Weiss et al.[80], glycolaldehyde is formed in amounts stoichiometrically equivalent to those of hydrogen peroxide. In the present study, glycolaldehyde was only detected in very low yield, and in every instance, the G-value was less than 0.01. The hydroxyhydroperoxide obtained under the present conditions may thus be the precursor of glycolaldehyde:

$$\begin{matrix} CH_2 \cdot CH_2 \\ | \quad | \\ OH \quad OOH \end{matrix} \longrightarrow \begin{matrix} CH_2 \cdot CHO \\ | \\ OH \end{matrix} + H_2O \qquad (63)$$

A rather similar reaction scheme involving an unstable hydroxyhydroperoxide has been previously suggested for the aqueous benzene-oxygen system[54]. If a corresponding sequence of reactions occurs in the present system, scission of the hydroperoxide would result in the formation of two molecules of formaldehyde:

$$\begin{matrix} CH_2 \cdot CH_2 \\ | \quad | \\ OH \quad OOH \end{matrix} \longrightarrow 2\ HCHO + H_2O \qquad (64)$$

Whether glycolaldehyde or β-hydroxyethylhydroperoxide is in fact formed apparently depends on the precise experimental conditions.

(c) Additives

Formaldehyde, G(HCHO) = 5.70, and acetaldehyde, $G(CH_3CHO)$ = 6.35, are the major products on irradiation of ethylene-oxygen solutions in the presence of ferrous ions

(10^{-3}M). Under these conditions, the yield of ferric ions was determined as $G(Fe^{3+}) = 26.95$. Weiss et al.[80] have suggested a probable mode of formaldehyde formation according to the reaction scheme:

$$HOCH_2CH_2O_2 + Fe^{2+} + H^+ \longrightarrow HOCH_2CH_2OOH + Fe^{3+}$$

$$HOCH_2CH_2OOH + Fe^{2+} \longrightarrow HOCH_2CH_2O + OH^- + Fe^{3+}$$

$$HOCH_2CH_2O \longrightarrow HOCH_2 + HCHO$$

$$HOCH_2O_2 + Fe^{2+} + H^+ \longrightarrow HOCH_2OOH + Fe^{3+}$$

$$HOCH_2OOH + Fe^{2+} \longrightarrow HOCH_2O + OH^- + Fe^{3+}$$

$$HOCH_2O + Fe^{2+} + H^+ \longrightarrow HCHO + H_2O + Fe^{3+}$$

In the absence of ethylene, one hydroxyl radical produces one ferric ion; in the presence of ethylene and oxygen there is a net increase of 4 ferric ions per hydroxyl radical, i.e., 2 ferric ions formed additionally per 1 molecule of formaldehyde. Acetaldehyde may be accounted for by a similar reaction scheme:

$$HO_2CH_2CH_2 + Fe^{2+} + H^+ \longrightarrow CH_3CH_2OOH + Fe^{3+}$$

$$CH_3CH_2OOH + Fe^{2+} \longrightarrow CH_3CH_2O + OH^- + Fe^{3+}$$

$$CH_3CH_2O + Fe^{2+} + H^+ \longrightarrow CH_3CHO + Fe^{3+} + H_2$$

In this instance, there is no change in the oxidation yield of ferric ions due to the presence of ethylene. The overall increase in $G(Fe^{3+})$ should therefore be equal to $2G(HCHO)$, i.e.,

$$G(Fe^{3+}) = 15.5 + 2G(HCHO) = 15.5 + 11.4 = 26.9$$

This value agrees well with the measured yield, $G(Fe^{3+})$ = 26.95.

(d) Summary

In an earlier Section, the radiation-induced oxidation and autoxidation processes occuring in other organic systems have been compared. In the present context, the true distinction is between low and high rates of initiation, since the propagation steps for both types of reaction may be indeed the same. At a dose-rate of ca. 10^5 rads/hr., the rate of radical formation in a solution corresponds to $1 - 2 \times 10^{-7}$ gm. radicals $litre^{-1}$ $sec.^{-1}$ This initiation rate is very small, however, compared with those used in liquid phase oxidations, e.g., the autoxidation of cumene initiated by benzoyl peroxide, where a value of 10^{-5} gm.radicals $litre^{-1}$ $sec.^{-1}$ is not unusual. Since termination is almost certainly bimolecular, there will be even less chain character in the oxidation of ethylene in aqueous solution at the more usual chemical initiation rates.

This work has thus provided no evidence that long chains are set up during the radiation-induced oxidation of ethylene. This is presumably due to the fact that the normal chain-propagating radicals rapidly combine with oxygen to form more highly oxygenated radicals and molecules. The principal fate of these species is evidently breakdown to smaller oxygenated products without propagation of a chain. This elimates the suggestion put forward by Henley et al.[79] that the radiation-

induced oxidation of ethylene in aqueous solution takes place by a mechanism involving long chains.

The most probable initial reactions in the oxygenated system may therefore be summarised as follows:

(i) in neutral solution,

$$e + O_2 \longrightarrow O_2^-$$

$$OH + CH_2 = CH_2 \longrightarrow HOCH_2\dot{C}H_2$$

$$O_2^- + CH_2 = CH_2 \longrightarrow \left[CH_2CH_2O_2\right]^-$$

$$HOCH_2\dot{C}H_2 + O_2 \longrightarrow HOCH_2CH_2O_2$$

$$HOCH_2\dot{C}H_2 + O_2^- \longrightarrow \left[HOCH_2CH_2O_2\right]^-$$

$$\left[CH_2CH_2O_2\right]^- + H \longrightarrow CH_3CHO + OH^-$$

$$\left[HOCH_2CH_2O_2\right]^- + H_2O \longrightarrow HOCH_2CH_2O_2H + OH^-$$

$$HOCH_2CH_2O_2H \longrightarrow 2HCHO + H_2O$$

(ii) in acid solution,

$$H + O_2 \longrightarrow HO_2$$

$$OH + CH_2 = CH_2 \longrightarrow HOCH_2\dot{C}H_2$$

$$HO_2 + CH_2 = CH_2 \longrightarrow HO_2CH_2\dot{C}H_2$$

$$HO_2CH_2\dot{C}H_2 \xrightarrow{XH} CH_3CHO + H_2O + X$$

$$HOCH_2\dot{C}H_2 + O_2 \longrightarrow HOCH_2CH_2O_2$$

$$HO_2CH_2\dot{C}H_2 + O_2 \longrightarrow HO_2CH_2CH_2O_2$$

$$HO_2CH_2CH_2O_2 \xrightarrow{XH} CH_3CHO + H_2O + O_2 + X$$

$$HOCH_2CH_2O_2 \xrightarrow{XH} HOCH_2CH_2O_2H + X$$

$$HOCH_2CH_2O_2H \longrightarrow 2HCHO + H_2O$$

BIBLIOGRAPHY

1. Walling, C., 'Free Radicals in Solution', Wiley, 1957, Chapt. 9.

2. Davies, A.G., 'Organic Peroxides', Butterworths, London, 1961.

3. Allen, A.O., 'The Radiation Chemistry of Water and Aqueous Solutions', Van Nostrand, 1961.

4. Weiss, J., Nature 153, 748 (1944).

5. Allen, A.O., Hochanadel, C.J., Ghormley, J.A., and Davies, T.W., J.Phys.Chem. 56, 575 (1952).

6. Barr, N.F., and Allen, A.O., J.Phys.Chem. 63, 928 (1959).

7. Czapski, G., and Schwarz, H.A., J.Phys.Chem. 66, 471 (1962).

8. Hart, E.J., and Boag, J.W., J.Am.Chem.Soc. 84, 4090 (1962)

9. Keene, J.P., Nature 197, 47 (1963).

10. Rigg, T., Stein, G., and Weiss, J., Proc.Roy.Soc.A 211, 375 (1952).

11. Dainton, F.S., and Watt, W.S., Nature 195, 1294 (1962).

12. Hart, E.J., Gordon, S., and Hutchinson, D.A., J.Am.Chem.Soc. 74, 5548 (1952).

13. Hart, E.J., Gordon, S., and Hutchinson, D.A. J.Am.Chem.Soc. 75, 6165 (1953).

14. Scholes, G., and Weiss, J., Radiation Research, Suppl.1, 177 (1959).

15. Cottrell, T.L., 'The Strength of Chemical Bonds', 2nd.ed., Butterworth, 1958, p.271.

16. Jayson, G.G., Scholes, G., and Weiss, J., J.Chem.Soc.1957, 1358.

17. Bach, N., Proc.1st Intern.Conf. Peaceful Uses of Atomic Energy, Geneva, 1955, 7, 538.

18. Bach, N., Radiation Research, Suppl. 1, 190 (1959).

19. Bach, N., and Popov, N.I., Symp.Rad.Chem.Acad.Sci., USSR,156(1952).

20. Bach, N., and Saraeva, V.V., Zhur.Fiz.Khim. 32, 209 (1958).

21. Dobson, G., and Hughes, G., Proc.Chem.Soc. 1963, 109.

22. McCarthy, R.L., and MachLachlan, A., J.Chem.Phys. 35, 1625 (1961).

23. Emanuel, N.M., Doklady Akad. Nauk SSSR.111,1286(1956).

24. Proskurnin, M.A., Khmel'nitskii, Yu.L., Barelko, E.V., Slepneva, A.T., and Melekkhonova, I.I., Doklady Akad. Nauk SSSR.112, 886(1957).

25. Emanuel, N.M., Blyumberg, E.A., Ziv., D.M., and Pikaeva, V.L., Doklady Akad. Nauk SSSR.119,1183(1958).

26. Churchill, S.W., Weir, A., Gealer, R.L., and Kelley,R.J., Ind.Eng.Chem. 49, 1419 (1957).

27. Cullen, R.E. and Gluckstein, M.E., 5th Symposium on Combustion, Reinhold, New York, 569 (1955).

28. Johnson, G.R.A., and Weiss, J., Chem. and Ind. 13, 358 (1955).

29. Phung, P.V., and Burton, M., Radiation Research. 7, 199 (1957).

30. Brun, M., and Montarnal, R., Compt.rend. 247, 2361 (1958).

31. Clay, P.G., Weiss, J., and Whiston, J., Proc.Chem.Soc. 1959, 125.

32. Scholes, G., and Weiss, J., Nature 185, 305 (1960).

33. Clay, P.G., Johnson, G.R.A., and Weiss, J., J.Phys.Chem. 63, 862 (1959).

34. Bach, N.A., and Saraeva, V.V., Symp.Rad.Chem.Acad.Sci.,USSR,175(1955).

35. Bach, N.A., and Sorokin, Yu.I., Symp.Rad.Chem.Acad.Sci.,USSR,163(1955).

36. Kailan, A., Sitzber.Akad.Wiss.Wien.Math.Naturw. Klasse.Abt.IIa, 143, 163 (1934).

37. Loiseleur, J., and Latarjet, R., Bull.Soc.Chim.Biol. 24, 172 (1942).

38. Loiseleur, J., Latarjet, R., and Crovisier, C., Compt.Rend.Soc.Biol. 136, 57 (1942).

39. Taub, I.A., and Dorfman, L.M., J.Am.Chem.Soc. 84, 4053 (1962).

40. Fricke, H., Hart, E.J., and Smith, H.P., J.Chem.Phys. 6, 229 (1938).

41. Serat, W.F., and Mead, J.F., Radiation Research 11, 370 (1959).

42. Hart, E.J., J.Am.Chem.Soc. 73, 68 (1951).

43. Hart, E.J., J.Phys.Chem. 56, 594 (1952).

44. Hart, E.J., J.Am.Chem.Soc. 76, 4198, 4312 (1954).

45. Smithies, D., Radiation Research. 9, 185 (1958).

46. Hart, E.J., J.Am.Chem.Soc. 81, 6085 (1959).

47. Smithies, D., and Hart, E.J., J.Am.Chem.Soc. 82, 4775 (1960).

48. Slover, H.T., and Dugan, L.R., J.Am.Oil Chem.Soc. 34, 333 (1957).

49. Dugan, L.R., and Landis, P.W., J.Am.Oil Chem.Soc. 33, 152 (1956).

50. Swallow, A.J., 'Radiation Chemistry of Organic Compounds',Pergamon Press, 1960,p.140.

51. Baxendale, J.H. and Smithies, D., J.Chem.Soc. 1959, 779.

52. Barelko, E.V., Kartasheva, L.I., Novikov, P.D., and Proskurnin, M.A., Proc.1st All-Union Conf.on Rad-Chem. 1957, 89.

53. Dorfman, L.M., Taub, I.A., and Buehler, R.E., J.Chem.Phys. 36, 3051 (1962).

54. Daniels, M., Scholes, G., and Weiss, J., J.Chem.Soc. 1956, 832.

55. Durup, J., J.Chim.Phys. 54, 739 (1957).

56. Stein, G., and Weiss, J., J.Chem.Soc. 1951, 3265.

57. Slovokhotova, N.A., and Karpov, W.L., 'Sbornik rabot po radiotzionoi khimii', Moscow, 1955, p.196.

58. Alexander, P., and Toms, D., J.Polymer. Sei. 22, 343 (1956).

59. Durup, J., J.Chim.Phys. 54, 739 (1957).

60. Durup, J., 'Organic Peroxides in Radio-biology' (ed. by R.Latarjet), Pergamon Press, 1958, p.27.

61. Hengleim, A., Schneider, C., and Schnabel, W., Z.Physik.Chem. (Frankfurt), 12, 339 (1957).

62. Alexander, P., and Charlesby, A., J.Polymer. Sci. 23, 355 (1957).

63. Bateman, L., Quart. Revs. 8, 147 (1954).

64. cf. Ref. 1., p. 405.

65. Gray, J.A., J.Chem.Soc. 1952, 3150.

66. Bell, E.R., Dickey, F.H., Raley, J.H., Rust, F.F. and Vaughan, W.E., Ind.Eng.Chem. 41, 2597 (1949).

67. Farkas, A., and Passaglia, E., J.Am.Chem.Soc. 72, 3333 (1950).

68. Engler, C., Ber. 30, 1669 (1897); 31, 3046 (1898); 33, 1090 (1900)

69. Farmer, E.H., and Sundralingham, A., J.Chem.Soc. 1942, 121.

70. Mayo, F.R., J.Am.Chem.Soc. 80, 2497 (1958).

71. Twigg, G.H., Chem.Eng.Sci. 3 (Suppl.), 5 (1954).

72. Russell, G.A. J.Chem.Educ. 36, 111 (1959).

73. Bolland, J.L., and Cooper, H.R., Nature 172, 413 (1953).

74. Bäckström, H.L.J., Z.physik.Chem. B25, 99 (1934).

75. Walling, C., and Buckler, S.A., J.Am.Chem.Soc. 77, 6032 (1955).

76. Serif, G.S., Hunt, C.F., and Bourns, A.N., Can.J.Chem. 31, 1229 (1953).

77. Notley, N.T., Trans. Farad.Soc. 58, 66 (1962).

78. Henley, E.J., and Schwartz, J.P. J.Am.Chem.Soc. 77, 3167 (1955).

79. Henley, E.J., Schiffries, W.P., and Barr, N., Am.Inst.Chem.Eng.J. 2, 211 (1956).

80. Clay, P.G., Johnson, G.R.A., and Weiss, J., J.Chem.Soc. 1958, 2175.

81. cf. Ref. 3., p.143.

82. Halmshaw, R., and Knapp, R., U.K. (Ministry of Supply) Report ARE 3/54 (1954).

83. Waterman, H.I., Hessles, W.J., and van Steamis, J., J.Inst.Petroleum 33, 254 (1947).

84. Hessels, W.J., van Krevelen, D.W., and Waterman, H.I., Rec.trav.chim. 59, 697 (1940).

85. Bone, W.A., and Townend, D.T.A., Flame and Combustion in Gases, Longmans, Green & Co.Ltd., 1927,p.93.

86. Coward, H.F., and Jones, G.W., U.S. Bureau of Mines,Bulletin 503,1952.

87. Teranishi, H., Rev.Phys.Chem.Japan. 29, 30 (1959).

88. Jost, W., Explosion and Combustion Processes in Gases,McGraw-Hill,London,1946,p.111.

89. Jones, G.W., Yant, W.P., Miller, W.E., and Kennedy,R.E., U.S. Bureau Mines Repts. Invest No.3278, 1935.

90. Jones, G.W., Kennedy, R.E., and Thomas, G.J., U.S. Bureau Mines Tech.paper 653, 1943.

91. Williams, H.R., and Mosher, H.S., J.Am.Chem.Soc. 76, 2984 (1954).

92. Ekert, B., and Monier, R., Nature 184, B.A. 58 (1959).

93. Barusch, M.R., and Payne, J.Q., J.Am.Chem.Soc. 75, 1987 (1953).

94. MacNevin, W.M., and Urone, P.F., Anal.Chem. 25, 1760 (1953).

95. Seidell, A., Solubilities of Organic Compounds, Vol.II. Van Nostrand Co.Inc., 1941, p.94.

96. Handbook of Chemistry and Physics, 41st Edn., Chemical Rubber Publ.Co.,1959-60,p.1706.

97. Hall, G.R., and Streat, M., J.Imp.Coll.Chem.Eng.Soc. 13, 80 (1962).

98. Fricke, H., and Morse, S., Phil. Mag. 1929, 129.

99. Dewhurst, H.A., Trans.Faraday.Soc. 48, 905 (1952).

100. Haybittle, J.L., Saunders, R.D., and Swallow, A.J., J.Chem.Phys. 25, 1213 (1956).

101. Bruschweiler, H., and Minkoff, G.J., Anal.Chim.Acta. 12, 186 (1955).

102. Knox, J.H., and Norrish, R.G.W., Proc.Roy.Soc. A221, 151 (1954).

103. Stern, V., and Polak, S., Acta.Physicochim.USSR.11, 797 (1939).

104. Gasparic, J., and Vecera, M., Coll.Czech.Chem.Commun. 22, 1426 (1957).

105. Roberts, J.D., and Green, C., J.Am.Chem.Soc. 68, 214 (1946).

106. Jones, L.A., Holmes, J.C., and Seligman, R.B., Anal.Chem. 28, 191 (1956).

107. Schmitt, W.J., Emil, S.J., Moricani, J., and O'Connor, W.F., Anal.Chem. 28, 249 (1956).

108. Johnson, G.R.A., and Scholes, G., Analyst 79, 217 (1954).

109. Openshaw, H.T., Qualitative Organic Analysis, C.U.P., 1955, p.46.

110. Shriner, R.L., Fuson, R.C., and Curtin, D.Y., Systematic Identification of Organic Compounds, Wiley, New York, 1956, p.283.

111. Raef, Y., Ph.D. Thesis, Imperial College, 1962.

112. Eegrive, E., Z.anal.chem. 110, 22 (1937).

113. Satterfield, C.N., Wilson, R.E., LeClair, R.M., and Reid, R.C., Anal.Chem. 26, 1792 (1954).

114. Grant, W.M. Anal.Chem. 20, 267 (1948).

115. Jones, L.R., and Riddick, J.R., Anal.Chem. 26, 1035 (1954).

116. Dechary, J.M., Kun, E., and Pitot, H.C., Anal.Chem. 26, 449 (1954).

117. Eisenberg, G.M., Ind.Eng.Chem.Anal. 15, 327 (1943).

118. Allen, A.O., Hochanadel, C.J., Ghormley,J.A., and Davies, T.W., J.Phys.Chem. 56, 575 (1952).

119. Cartlidge, J., and Tipper, C.F.H., Chem. and Ind. 1959, 852.

120. Abraham, M.H., Davies, A.G., Llewellyn, D.R., and Thain, E.M., Anal.Chim.Acta. 17, 499 (1957).

121. Minkoff, G.J., Bruschiweiler, H., and Salooja, K.C., Nature 172, 909 (1953).

122. Hashmi, M.H., and Cullis, C.F., Anal.Chim.Acta. 14, 336 (1956).

123. Pesez, P., and Ferrora, J., Bull.Soc.Chim.Biol. 39, 221 (1957).

124. Feigl, F., Spot Tests in Organic Analysis, 5th Ed., Elsevier, Amsterdam, 1957.

125. Stiller, M., Anal.Chim.Acta. 25, 85 (1961).

126. Collinson, E., and Dainton, F.S., Disc.Farad.Soc. 12, 212 (1952).

127. Snell, F.D., and Snell, C.T., Colorimetric Methods of Analysis,3rd Ed., van Nostrand, 1949, Vol.III, p.314.

128. Keene, J.P., Nature 188, 843 (1960).

129. Guggenheim, E.A.,Phil.Mag. 1926, 538.

130. Whiston, J., Ph.D. Thesis, University of Durham,1961.

131. Clay, P.G., Mohorcic, G., and Thomson, D.H., To be published.

132. Keene, J.P., Private communication.

133. Collinson, E., Dainton, F.S., Smith, D.R., and Tazuke, S., Proc.Chem.Soc.1962, 140.

134. Gordon, S., Hart, E.J., Matheson, M.S., Rabani, J.R., and Thomas, J.K., J.Am.Chem.Soc. 85, 1375 (1963).

135. Dainton, F.S., and Peterson, D.B., Proc.Roy.Soc. A267, 443 (1962).

136. Hart, E.J., To be published.

137. Walsh, A.D., Trans. Faraday.Soc. 42, 282 (1946).

138. Steacie, E.W.R., Atomic and Free Radical Reactions, 2nd.Edn., Reinhold, 1954, Vol.1,p.434.

139. Darwent, B. de B., and Roberts, R., Disc. Faraday. Soc. 14, 55 (1953).

140. Allen, P.E.M., Melville, H.W., and Robb, J.C., Proc.Roy.Soc.A 218, 311 (1953).

141. cf. Ref. 138, p.439.

142. Avramenko, L.E., and Lorentso, P.V., Doklady Akad.Nank.SSSR 67, 867 (1949).

143. Berces, T., and Trotman-Dickenson, A.F., J.Chem.Soc. 1961, 4281.

144. Schwarz, H.A., J.Phys.Chem. 66, 255 (1962).

145. Evans, M.G., Hush, N.S., and Uri, N., Quart. Rev. 6, 186 (1952).

146. Fricke, H., To be published.

147. Johnson, G.R.A., Scholes, G., and Weiss, J., Nature 177, 883 (1956).

148. Rosinger, S., and Mullner, St., Conference on Application of Large Radiation Sources in Industry, Salzburg, May 1963, CN - 14/56.

149. Dingledy, D.P., and Calvert, J.G., J.Am.Chem.Soc. 85, 856 (1963).

150. Johnson, G.R.A., and Weiss, J., Proc. Roy. Soc. A 240, 189 (1957).

151. Hart, E.J., and Platzman, R.L.,
'Mechanisms in Radiobiology', Vol. I,
Academic Press, 1961, p.228.

152. Steinberg, M., Colombo, P., Chapman, R.N., and Adler, G.,
BNL 740 (T-268), Radiation Processing
Report No. 4, July, 1962.

153. Finkelstein, A., and Noyes, W.A.,
Disc. Faraday Soc. 14, 76 (1953).

154. Avramenko, L.E., and Kolesnikova, R.V.,
Izvest.Akad.Nauk SSSR, Otdel.
Khim.Nauk 806, 989 (1960).

155. Mayo, F.R., and Miller, A.A.,
J.Am.Chem.Soc. 80, 2480 (1958).