

THE RADIOLYTIC OXIDATION OF METHANE

by

A. H. Rosen B.Sc.

A Thesis submitted for the degree of

Doctor of Philosophy

of the University of London.

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

ABSTRACT

Methane-oxygen mixtures have been irradiated using Co^{60} gamma radiation at 20°C and -78°C at 765 mm Hg pressure. The major products detected at 20°C were, methyl hydroperoxide, hydrogen, methanol, ethylene and ethane, and the initial G-values of formation were 3, 2.8, 1, 0.43, and 0.15 respectively. Very little formaldehyde was found present. Hydrogen peroxide was found present in large quantities when the irradiation was performed at -78°C , and the methyl hydroperoxide yield decreased. The ratio of $G(\text{H}_2\text{O}_2)$ to $G(\text{CH}_3\text{OOH})$ was found to depend upon the surface area of the irradiation vessel.

The dose-rates used in the experiments were between 0.4 and $9.3 \times 10^{14} \text{ eV/ml CH}_4/\text{min}$. No dose-rate effect was noted.

Methane was irradiated in the presence of small amounts of additives, to determine the relative rôles of radical and ionic reactions in the formation of products. The additives used were :- ethylene, propane, propylene, water vapour, ethylene plus oxygen, propane plus oxygen, propylene plus water vapour, and oxygen plus water vapour.

In general the majority of the products obtained can be accounted for by radical mechanisms. There is some evidence that oxygen may react with CH_5^+ , but in general reactions of this ion appear to be unimportant in radiolyses at low conversions.

Methane and methane plus oxygen were irradiated in the presence of mercury at 20°C. The product distribution obtained from methane was essentially the same as that obtained in the absence of mercury. The rate of formation of methyl hydroperoxide decreased by approximately 30% to $G(\text{CH}_3\text{OOH}) = 2.2$ in the presence of mercury, but no increase in the rate of formation of formaldehyde was noted. The presence of trace amounts of mercury are therefore unlikely to have much effect on the product distribution.

ACKNOWLEDGEMENTS.

The Author wishes to thank Dr. P. G. Clay for his invaluable guidance and encouragement throughout the work, and to record his appreciation for having been given the opportunity of carrying out research at the Nuclear Technology Laboratory by Professor G. R. Hall.

Acknowledgement is made to the Science Research Council for the Postgraduate Award.

CONTENTS.

	Page.
Abstract	2
Acknowledgements	4
Introduction	10
Chapter I Review of Previous Work	12
Chapter II Experimental Techniques	67
Chapter III Results	93
Chapter IV Discussion and Conclusions	126
Appendices	171
References	177

LIST OF FIGURES.

No.		Page.
1.	Variation of $G(C_2H_4)$ with pressure and conversion, from the radiolysis of methane, and methane plus propylene.	22
2.	Relative concentrations of the major ions formed from methane in the mass spectrometer, against ionisation chamber pressure of methane.	33
3.	Relative concentrations of the major ions from $CH_4+1\% C_2H_6$ in the mass spectrometer, against pressure of $CH_4+1\% C_2H_6$ in the source chamber.	33
4.	Relative concentration of the methyl, ethyl, and propyl ions, against total pressure of $CH_4+1\% C_3H_8$.	36
5.	Relative concentration of CH_5^+ and H_3O^+ , against total pressure of $CH_4+1\% H_2O$ in the source chamber.	36
6.	Calibration and Analysis Line.	89
7.	Vacuum Line.	90
8.	Trap used initially for product collection.	91
9.	Silica vessel used for polymer determinations.	91
10.	Sample vessel and connections to sampling valve.	91
11.	Gas sampling valve.	92
12.	Dose-yield plots for the major products from the radiolysis of methane at $20^\circ C$, and 765 mm Hg.	116

LIST OF FIGURES
(contd.)

No.		Page.
13.	Dose-yield plots for ethane, ethylene, propane, and iso-butane, from the radiolysis of methane at -78°C , 765 mm.	117
14.	Dose-yield plots for the major hydrocarbon products from the radiolysis of methane plus 0.026% oxygen, carried out at 20°C and 765 mm Hg.	118
15.	Dose-yield plots for methyl hydroperoxide and formaldehyde from the radiolysis of methane plus 0.026% oxygen at 20°C and 765 mm Hg.	119
16.	Dose-yield plots for methyl hydroperoxide and formaldehyde, from the radiolysis of methane plus 2% oxygen in the absence and presence of mercury, 20°C and 765 mm.	120
17.	First order plots for the methyl hydroperoxide product from the radiolysis of methane plus 2% oxygen, at 20°C and 765 mm Hg.	121
18.	First order plots for the reaction between methyl hydroperoxide and iodide reagent.	122
19.	Dose-yield plots for methyl and ethyl alcohol from the radiolysis of methane plus 2% oxygen and 1% water vapour, at 20°C and 765 mm Hg.	123
20.	G-values for the formation of hydrogen, ethane, and ethylene from the radiolysis of methane plus propane and oxygen, against additive concentration.	124
21.	Oxygen consumed in the radiolysis of methane plus 0.065% oxygen against dose received.	125
22.	Arrhenius plot for the formation of ethane	163

LIST OF TABLES.

No.		Page.
1.	Methane Mass Spectra at Various Pressures 10 ⁻⁴ to 2 mm Hg.	31
2.	Rate Constants for some Ion-molecule Reactions.	37
3.	G-values for some Major Primary and Secondary Ions in Methane.	38
4.	G-values for Product Formation from the Radiolytic Oxidation of Methane Using High Energy Electrons.	49
5.	G-values for the Major Products from the Radiolysis of Methane plus 10% Oxygen Using 4MeV Electrons and Co ⁶⁰ Gamma Radiation.	51
6.	G(-O ₂) based on the Oxygen found in the Products from the Radiolytic Oxidation of Methane.	54
7.	Comparison of the Dose-rates obtained using the Fricke, Nitrous Oxide, and Methane Dosimeters.	95
8.	Initial G-values for Hydrogen and the Hydro- carbon Products from the Radiolysis of Methane, and Methane plus Hydrocarbon Additives.	100
9.	G-values for the Hydrocarbon Products from Methane plus Oxygen Irradiated at 20°C and -78°C.	104
10.	G-values for the Oxygenated Products from Methane plus Oxygen Irradiated at 20°C and -78°C.	106

LIST OF TABLES
(contd.)

No.		Page.
11.	G-values for Initial Product Formation from the Radiolysis of Methane plus Various Additives.	112
12.	G-values for the Products Measured from the Radiolysis of Methane, and Methane plus Mercury, at 20°C.	115
13.	G-values Obtained Experimentally for Methyl Radical Formation from the Radiolysis of $\text{CH}_4 + \text{O}_2$, $\text{CH}_4 + \text{O}_2 + \text{C}_3\text{H}_8$, and $\text{CH}_4 + \text{O}_2 + \text{H}_2\text{O}$.	132
14.	G-values for Hydrogen and the Hydrocarbon Products from the Radiolysis of CH_4 , $\text{CH}_4 + \text{C}_2\text{H}_4$, and $\text{CH}_4 + \text{C}_3\text{H}_6$.	144
15.	G-values for Hydrogen, and the Major Hydrocarbon Products from the Radiolysis of CH_4 , $\text{CH}_4 + \text{H}_2\text{O}$, and $\text{CH}_4 + \text{O}_2 + \text{H}_2\text{O}$.	151
16.	G-values for Hydrogen and the Hydrocarbon Products from the Radiolysis of $\text{CH}_4 + \text{C}_2\text{H}_4$ and $\text{CH}_4 + \text{C}_2\text{H}_4 + \text{O}_2$.	156
17.	G-values for Hydrogen and the Major Hydrocarbon Products from the Radiolysis of CH_4 , $\text{CH}_4 + \text{O}_2$, $\text{CH}_4 + \text{NO}$.	158
18.	Initial G-values for the Formation of Hydrogen and the Major Hydrocarbon ^{Products.} from the Radiolysis of Methane at -78°C and 20°C.	161
19.	G-values for Polymer Formation and for Methane Consumption in the Radiolysis of Methane at -78°C and 20°C, and Methane plus Additives at 20°C.	16-

INTRODUCTION

The production of chemicals on an industrial scale using ionising radiation to promote the reactions has received considerable attention since the early 1950's. Few systems are suitable as the rate of formation of the products using radiation to initiate the reactions, is in most cases too low for the processes to be economic. The rate of formation of a compound as a result of depositing energy in a medium using radiation, is a function of the G-value of formation of that compound. The G-value is defined as the number of molecules of the particular species formed per 100 eV of energy deposited in the initial reactants.

Large scale radiation sources are isotopic sources, electrical machines, and chemonuclear reactors. The power output of the first two types mentioned is of the order of kw/hr, and these sources are only suitable for systems in which the product is produced via a chain reaction (the G-value being 10^3 or greater). For reactions which proceed with G-values of 10 or less only chemonuclear reactors can be considered for large scale production. Systems which have been considered in this context include:-

- a) Nitrogen fixation (1, 2)
- b) Carbon dioxide cracking using
nitrous oxide as a catalyst (2)

c) Ethylene glycol from ethanol (3)

d) Hydrazine from ammonia (3)

and recently

e) Methanol and formaldehyde from
the partial oxidation of methane (4)

Systems a) and e) are attractive since the raw materials can be obtained both cheaply and in large quantities.

Very little information was available about the products formed or the mechanisms of the radiolytic oxidation of methane. The work was intended to evaluate the yields of the major products, their G-values of formation, and at the same time to obtain information about the mechanisms of product formation in methane plus oxygen and in pure methane. The work is an extension to the studies being carried out at Imperial College on the irradiation of methane using fission fragments (4).

CHAPTER I

REVIEW OF PREVIOUS WORK

	Page.
Section 1. Radiation Chemistry of Methane.	
1.1 Introduction.	13
1.2 Radical Mechanisms.	17
1.3 Ionic Mechanisms.	28
Section 2. Radiation Chemistry of Methane plus Oxygen: Oxygenated Product Formation.	
2.1 Radical Mechanisms.	48
2.1.1 High Temperature Oxidation.	62
2.2 Ionic Mechanisms.	63

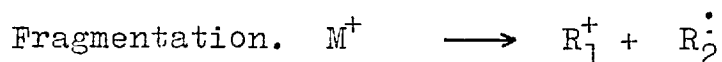
Section 1.1 Introduction.

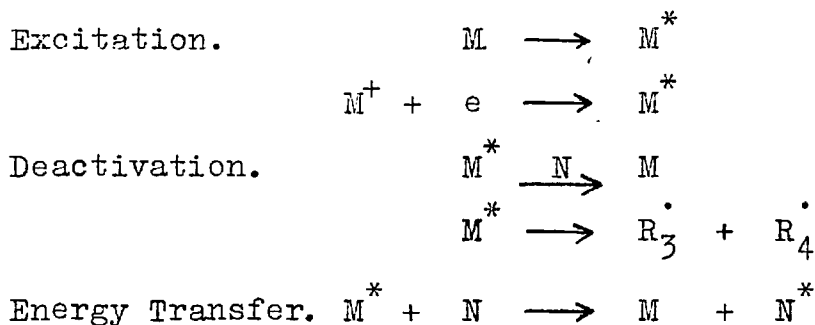
The interaction of gamma radiation with gases produces ionised and excited species by several mechanisms. There are three important ways by which the gamma photons lose their energy in passing through matter; Compton scattering, pair production, and photo-electric absorption. Co^{60} gamma radiation interacts with media of low atomic number by Compton scattering where the energy of the photon is lost by ejecting electrons from atoms by collision. The deflected photon may again collide with more atoms and eject electrons until its energy has been reduced to about 10 eV. The fast electrons ejected by the photons in turn interact to produce many more electrons. When the energy of the electrons is greater than the ionisation potential of the medium, ionisation and excitation can result. Slow electrons usually interact by knock-on collisions, which are far more effective in producing ionisation than the glancing collisions of the fast electrons. Eventually the energy of the electron falls below the lowest ionisation potential of the medium and the electrons then only cause excitation. Finally electron capture by attachment to molecules, or by positive ions, takes place. Attachment leads to negatively charged molecules, e.g. O_2^- , the neutralisation capture giving rise to highly excited species which may decompose.

The effect of radiation on a gaseous system is thus to cause ionisation and excitation of the molecules. The energy required to form an ion-pair (a positive ion and a negative counterpart) from molecules is of the order of 30 eV. The ionisation potential of most gases lies between half and one third of the energy required for ion-pair formation. This means that about half of the molecules receive energy but are not ionised. These molecules are referred to as excited species; they may be deactivated by emission of radiation, energy transfer, various radiationless transitions, or decompose to give radicals, atoms, or molecular compounds. It is generally accepted that there are approximately as many excited species as there are ions.

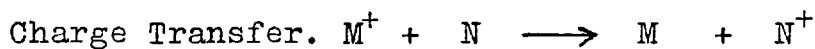
Energy transferred to a molecule in excess of the lowest ionisation potential does not necessarily ionise it (5); dissociation or internal conversion may result. In a simple molecule such as methane, dissociation rather than internal conversion will occur.

The above processes may be summarised by the following general reactions:-

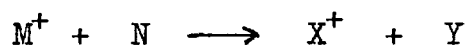




Positive ions may take part in other reactions prior to neutralisation such as charge transfer, and ion-molecule reactions.



Ion-molecule reaction.



Product formation in a medium subjected to ionising radiation arises from reactions of the species produced by the radiation. These species, (ions, excited molecules, free radicals, and atoms,) may react with one another, or with the molecules of the medium to give either intermediate compounds or the final products observed. Mechanisms which have been proposed for product formation range from purely free radical, to completely ionic schemes. Evidence for the former is based on experiments where the medium is irradiated in the presence of a free radical scavenger. The removal of the radicals by the scavenger produces a marked effect on the product distribution. Mass spectrometric studies at pressures up to 2 mm Hg, and the scavenging of ions formed during radiolysis, conclusively

demonstrate the occurrence of ion-molecule reactions.

The rôles of ions and radicals in product formation are difficult to separate since on decomposition or neutralisation ions can give rise to free radicals. In general the yields of the products from the radiolyses can not be satisfactorily explained on the basis of purely free radical or ionic mechanisms. Both processes undoubtedly occur in irradiated gaseous systems.

In view of the fact that both free radical and ionic processes are important in the formation of products in the radiolysis of gaseous systems, this survey of previous work has been divided into two sections. The first deals with the evidence for radical processes leading to the formation of products. The second part considers the evidence for ionic schemes. The mechanism for polymer formation has been included in the latter section since it is most probably formed via ionic reactions.

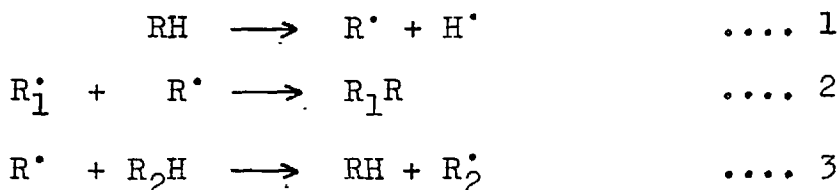
Section 1.2 Radical Mechanisms.

The effects of radiation on methane were first studied in detail by Lind and Bardwell in 1926 (6). Very large doses were used, conversions being as high as 75%. The products noted were hydrogen and saturated hydrocarbons and a polymeric material. No unsaturated products were found to be present. Neutralisation of an ion-complex $\text{CH}_4 \cdot \text{CH}_4^+$ was put forward to explain the formation of the products.

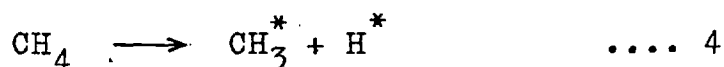
The ion-complex idea was questioned by Honig and Sheppard (33). The removal of ions during radiolysis using electro-static fields, only changed the reaction rate by 30%. The product distribution obtained using deuteron radiation was similar to that observed by Lind. The similarity between radiolysis and excitation of methane using electrons having energies too low to cause ionisation, and mercury sensitised photolysis, led to the suggestion that the products were formed largely by radical routes.

The addition of radical scavengers to methane, such as iodine (9), hydrogen iodide (7,8), and nitric oxide (35, 36), prior to radiolysis, confirmed that free radicals were formed in the radiolysis. In the presence of the scavengers the yields of hydrogen and the saturated hydrocarbons were markedly reduced, and ethylene was found to be the major hydrocarbon product. A free

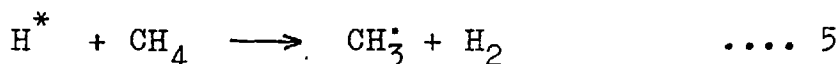
radical scheme was proposed for product formation.



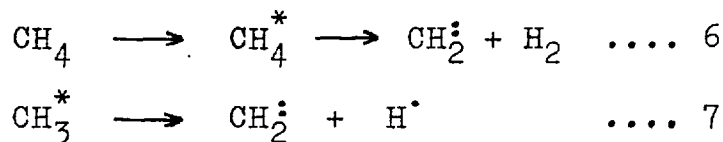
The production of a 'hot' methyl radical and hydrogen atom from the decomposition of methane was suggested.



The hot hydrogen atom then abstracted hydrogen from methane

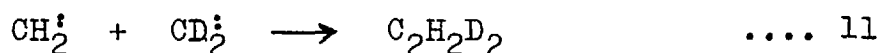
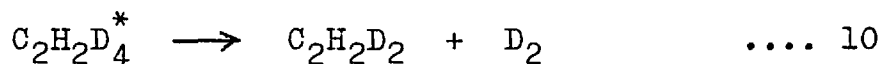
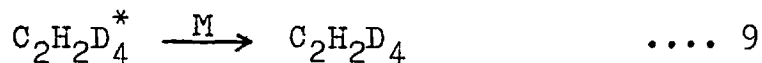
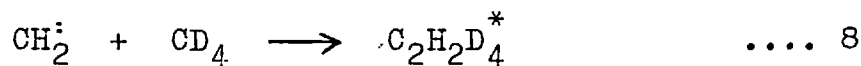


Methylene radicals were thought to arise from the decomposition of an excited methane molecule, or the 'hot' methyl radicals produced by reaction 4.

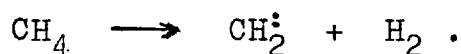


Reaction 6 was also proposed by Manton (80) for the production of methylene radicals. Evidence for neutral excited molecule decomposition yielding methylene radicals, was obtained by Manton (37), Walker and Back (28), and Ausloos (25), both in the photolysis and radiolysis of methane. Analysis of the ethane yield from $\text{CD}_4 + \text{CH}_4$ (1 to 1 ratio) radiolysis (32), showed a substantial part of the yield to consist of $\text{C}_2\text{H}_2\text{D}_4$ and $\text{C}_2\text{D}_2\text{H}_4$. In the presence of iodine, a scavenger for methyl radicals,

$C_2H_2D_2$ constitutes about 13% of the ethylene yield. Also, in the radiolysis of $CD_4 + CH_4 + NO$ the ethanes formed were found to consist almost entirely of $C_2H_2D_4$, $C_2D_4H_2$, C_2H_6 and C_2D_6 . This isotopic distribution could only be accounted for on the basis of their being formed by methylene insertion into methane. The excited ethane molecule formed is either stabilised by collision, or may dissociate to give ethylene. Ethylene may arise from the combination of two methylene radicals.

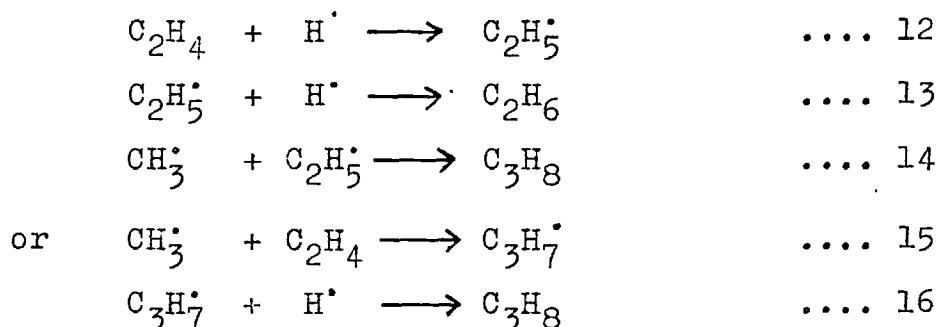


That the major part of the hydrogen yield from the radiolysis of $CD_4 + CH_4 + I_2$ (23), was found to consist of molecular hydrogen H_2 and D_2 , and not HD , was further evidence for the occurrence of the reaction



The presence of hydrogen atoms as well as hydrogen molecules was demonstrated by Yang (35, 36). Using nitric oxide as a scavenger the hydrogen yield decreased by about 45% compared to that obtained from pure methane. Thus hydrogen molecules are formed in the radiolysis of methane. Further studies were carried out by Sieck and Johnson (16) using ethylene as the hydrogen atom

scavenger. With small concentrations of the additive the hydrogen yield decreased, and that of ethane and the higher hydrocarbons increased. These observations were explained on the basis of ethyl radical formation from hydrogen atoms plus ethylene. The ethyl radical being considered the precursor of ethane.

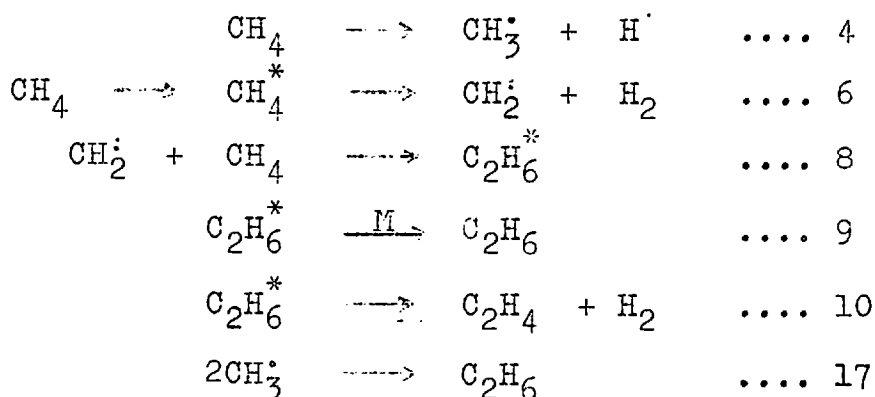


The effect of ethylene on the system seems to have been oversimplified, reactions 13 and 16 being unlikely, since all the hydrogen atoms are scavenged by the ethylene. The results obtained were not the initial G-values, and the G-values do not agree with those noted by Hummel (20). Using 4 MeV electrons, at very low conversions (less than 0.01%) Hummel investigated the rôle of unsaturated compounds in the radiolysis of methane. Ethylene was found to be a major product from the radiolysis of methane irradiated to low conversions. A small amount of acetylene was also observed in pure methane. Larger amounts of acetylene were noted from the radiolysis of methane under dynamic conditions by passing the gas through a beam of electrons. From results of irradiations carried out in the presence of unsaturated hydrocarbons, it was concluded that product

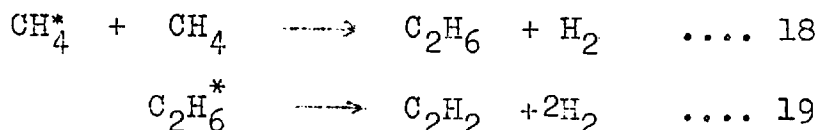
formation in pure methane proceeded to a large extent via the primary formation of acetylene and ethylene. With propylene present to protect the ethylene from hydrogen atom attack, the initial G-value for ethylene formation was found to be 3.4 (Fig.1 p.22). The G-value for ethylene formed in the radiolysis of pure methane tended towards this value at low conversions and low pressures. The G-value for acetylene was stated to be as high as 0.3.

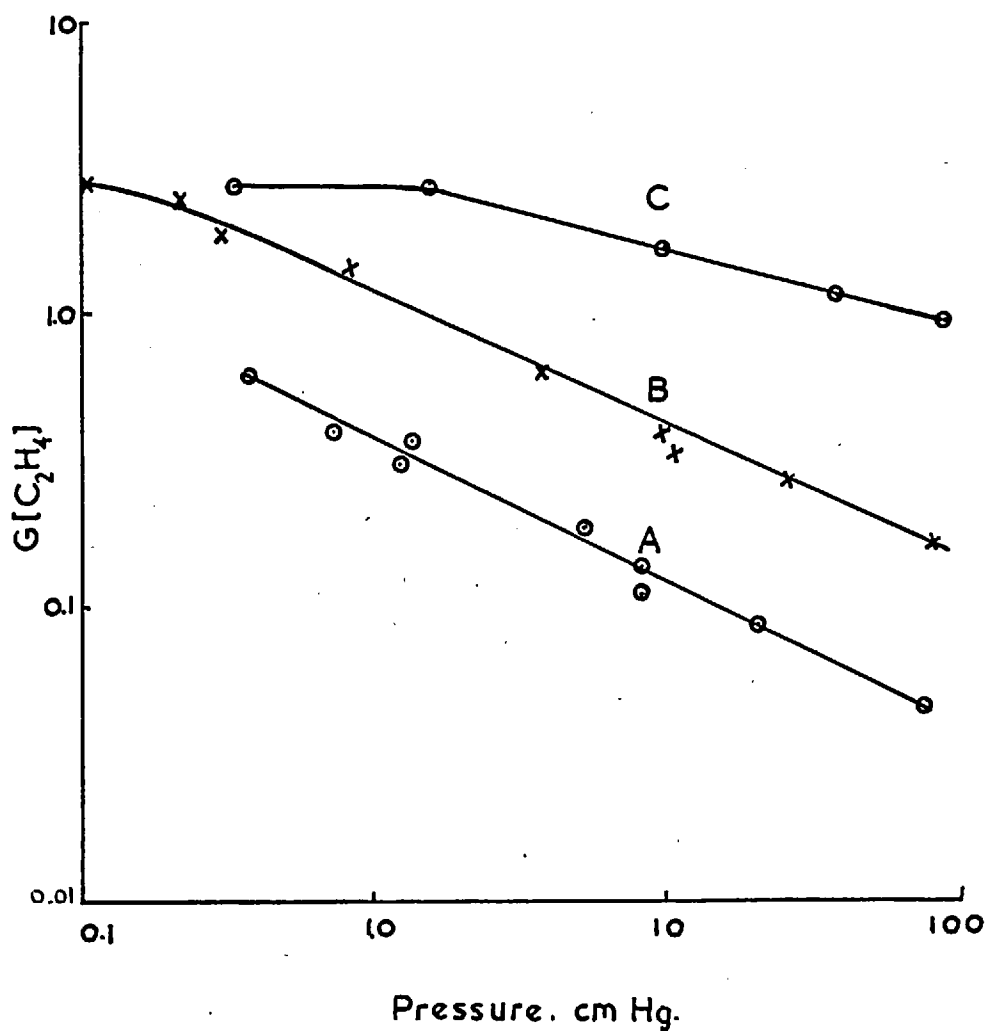
Very small amounts of acetylene have been observed in the radiolysis of methane at high dose-rates, of the order of 10^{21} eV/g/min (38).

A small yield of propylene was noted in methane plus oxygen as a radical scavenger (20). The mechanism proposed for product formation was:



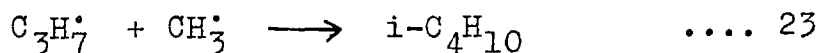
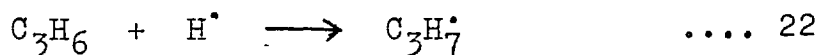
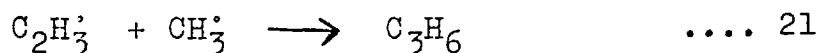
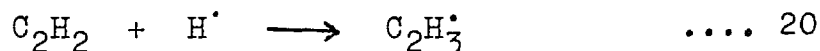
and possibly



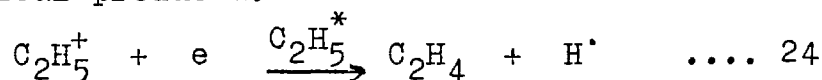


Variation of $G[C_2H_4]$ with pressure from the radiolysis of pure methane (curve A, 0.16% conversion : curve B, 0.04%) and from methane plus 1% CH_3 (curve C, 0.01% conversion).

Fig.1

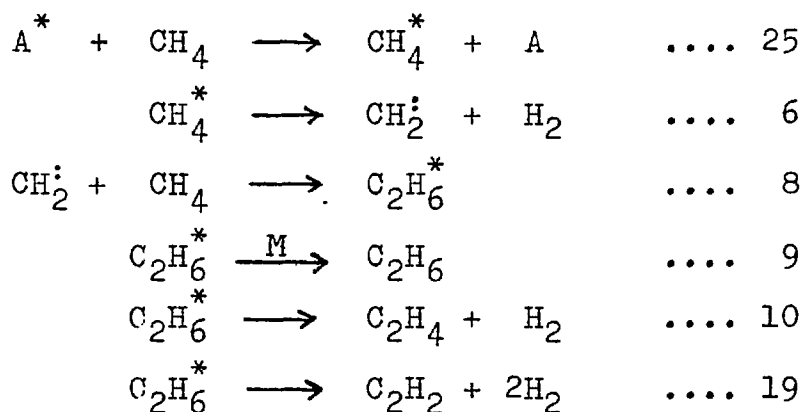


Neutralisation of the ethyl ion C_2H_5^+ was proposed, ethylene and hydrogen atoms being formed from the excited ethyl radical produced.

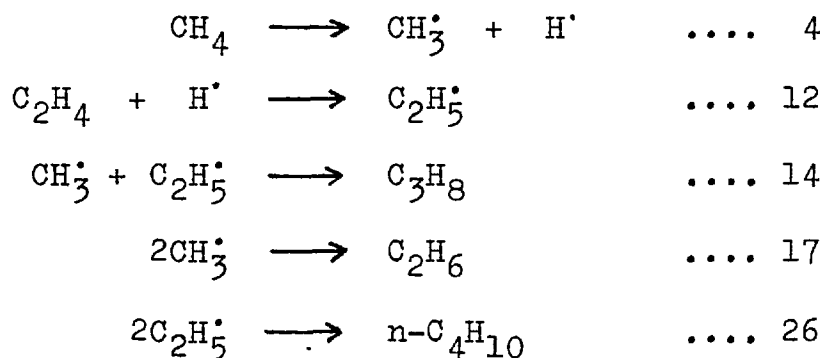


The relative rôles of ions and free radicals in the mechanism of product formation in methane radiolysis, was the subject of a paper by Aquilanti (21). Methane was irradiated at 100 mm Hg total pressure in the presence of a large excess of argon, krypton, or xenon, and plus small amounts of radical scavengers. As was observed by Lampe (18) ethane and propane were found to be formed simultaneously in pure methane, and in methane plus argon and krypton. Results obtained in the presence of nitric oxide indicated that hydrogen was probably produced via reactions of the primary products of radiolysis. Increases in various product yields in the rare-gas-methane radiolyses confirmed that charge and energy transfer reactions occurred between the rare gas and methane, the nature and magnitude of the reaction depending upon the rare gas. These observations were endorsed by Hummel (29), who used argon and xenon as the additives. At high argon

concentrations the ethylene yield was found to increase and the concentrations of the saturated hydrocarbon products to decrease. This was thought to be due to a decrease in the hydrogen atom concentration, from the diminished importance of the reaction $\text{CH}_4 \longrightarrow \text{CH}_3^\cdot + \text{H}^\cdot$. The results were partially explained on the basis of energy transfer from argon to methane, yielding methylene rather than methyl radicals.



Since the concentration of methyl radicals and hydrogen atoms was suppressed, the rôles of reactions 12, 14, 17 and 26 were diminished.

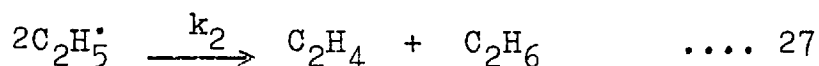
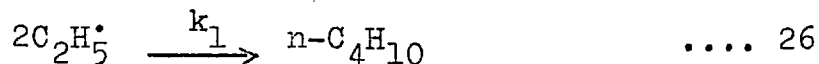


Iso-butane was considered to be formed by radical reactions starting from acetylene as previously

outlined (page 23). The yield of iso-butane was thought to be likely to remain unaffected, since the rate of production of acetylene should not change in the presence of argon. As there is a decrease in both methyl radical and hydrogen atoms, the constancy of the iso-butane yield is difficult to explain on this basis. Also, the presence of acetylene in methane radiolysis was questioned by Johnsen (39), who was unable to detect any at either high or low dose-rates. Hummel repeated the experiments on pure methane at a dose-rate of about 10^{21} eV/ml/min, and confirmed the presence of acetylene using a mass spectrometer to analyse the products. The G-value obtained was lower than that previously measured ($G(C_2H_2) = 0.01$) (29).

From these results it would appear that the acetylene yield is much greater than the steady-state yield, or not formed in other than trace amounts, or that iso-butane is not formed by the proposed reaction scheme.

The formation of normal butane from ethyl radicals is not the only reaction possible. A disproportionation reaction giving ethane and ethylene has been reported (40).

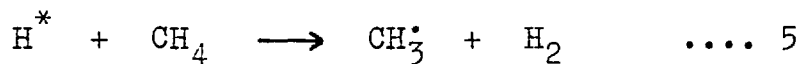


The ratio of the rate constants k_2/k_1 was given as 0.14.

The presence of hydrogen atoms and molecules in methane radiolysis has been demonstrated by Yang (35),

Sieck and Johnsen (16), and Hummel (20). In the presence of radical scavengers the hydrogen yield is reduced by about half. The production of molecular hydrogen has been discussed (page 19), but the rôle of hydrogen atoms is not yet clear.

Hydrogen atom abstraction reactions have been shown (41) to be unimportant at temperatures less than about 150°C. Reaction 5 is therefore unlikely to occur at room temperature.



The formation of HD from $\text{CH}_4 + \text{CD}_4$ (23) may well in part arise from reactions between hydrogen and deuterium atoms, since it is apparent that $G(\text{H})$ is greater than $G(\text{C}_2\text{H}_4) + G(\text{C}_2\text{H}_2) + G(\text{C}_3\text{H}_6)$. That there is an increase in the product yields on adding unsaturated hydrocarbons to methane prior to irradiation, is also an indication of the presence of hydrogen atoms. But the magnitude of the contribution of the reactions between the hydrogen atoms and the unsaturated compounds towards the increased yields is not known.

The formation of products in the photolysis and radiolysis of methane, where the energy of the radiation is such that ions are not formed, or where the ions that have been formed are removed by ion scavengers, undoubtedly proceeds via a free radical mechanism. The decomposition of methane by electrons leads to the formation of methyl

and methylene groups and hydrogen atoms and molecules. Reactions leading to product formation include methylene insertion into methane, resulting in ethane, hydrogen, and ethylene; and methyl radical combination giving ethane (some of which may decompose to give ethylene and hydrogen molecules). Ethyl radicals formed from ethylene plus hydrogen atoms, react mutually or with methyl radicals to yield normal butane and propane respectively. Some ethane and ethylene may be formed by a disproportionation reaction of the ethyl radicals.

Hydrogen is derived from reactions between hydrogen atoms, and directly from the decomposition of excited methane and ethane.

Other higher hydrocarbon products, which are formed in negligible amounts, are the result of free radical reactions.

The formation of both ethane and propane simultaneously is in accord with a free radical process for their production.

Radical scavengers such as nitric oxide and oxygen, have been assumed to remove the free radicals produced during the radiolyses, without having any effect on the production of these species. The validity of this assumption has not been established. That the radiation yield of the methyl radicals can be estimated by the effect of oxygen or nitric oxide on the product yields, must therefore be questioned.

Section 1.3 Ionic Mechanisms

In systems in which electrically charged species are present, the relative concentrations of the charged compounds may be determined using a mass spectrometer. The ions are separated and identified according to their ratio of mass to charge.

The principle in mass spectral analysis is to ionise the material using electrons, generally of 70 eV energy, and analyse the ions formed. Mass spectrometry may thus in some aspects be regarded as a special branch of radiation chemistry. The analyses can however only be carried out at low pressures, 10^{-8} to 2mm Hg, when the collisions between the ions and molecules present are few. At the lower pressures only the primary ions are observed. At 1 to 2 mm Hg pressure, an ion will undergo about 50 collisions during its residence time in the mass spectrometer, and secondary ions formed by the resulting collisions are observable.

The residence time of an ion in the mass spectrometer is about 10^{-5} second, and slow reactions between ions and molecules will not be observed. In a gas being irradiated at atmospheric pressure the slow reactions may be as important as the fast ion-molecule reactions which occur.

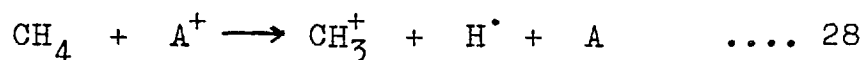
The relative concentrations of the ions depend upon the ionisation potentials of the parent molecule and the

electron energy. At high enough energies all of the possible decomposition products are obtained. The relative concentrations of the ionic species formed using 70 eV electrons, may not be the same as that produced in radiolysis by the more energetic electrons produced by gamma rays of 1 MeV energy. Excited species are also formed in radiolysis, and reactions of these species have to be considered.

In spite of the above differences between gas phase radiolysis at 760 mm Hg, and mass spectra obtained at 0.1 mm Hg, the latter are useful in interpreting the product yields obtained in radiolysis.

The possibility of ion-molecule reactions taking part in product formation was first proposed by Lind in 1926 (6). The formation of the ion-molecule complex $\text{CH}_4 \cdot \text{CH}_4^+$ was postulated, and neutralisation of this complex was thought to form ethane and hydrogen.

Product formation in the radiolysis of methane by a series of ion-molecule reactions, was proposed by Meisels et al. (7). From a subsequent study using a mass spectrometer to identify the ions formed, several ion-reactions were confirmed. Evidence for a charge transfer reaction from argon to methane was obtained.



Similar reactions were observed for krypton and xenon in mixtures with hydrocarbons. A large number of papers have since been published confirming Meisel's observations, and noting the occurrence of other reactions (9, 10, 11, 12, 13).

The primary ions obtained using, 70 eV electrons to ionise methane, at the lowest pressures are; CH_4^+ , CH_3^+ , and CH_2^+ . Small amounts of CH^+ and C^+ have also been reported (14, 15). CH_4^+ and CH_3^+ accounted for 85% to 90% of the total ionic yield. The mass spectra of methane obtained by Munson (15), has been reproduced in Table 1 page 31. At higher pressures in the source chamber of the mass spectrometer, the secondary ions CH_5^+ and C_2H_5^+ account for about 70% of the ion yield (15); smaller amounts of C_2H_2^+ , C_2H_3^+ , C_2H_4^+ , C_3H_5^+ and C_3H_7^+ are present. The relative distribution of these ions has been plotted in Fig.2 page 33. From these observations, the reaction of the ions CH_4^+ and CH_3^+ with methane to give CH_5^+ and C_2H_5^+ respectively, was deduced. Further reactions of the other ions were proposed (15).

Primary Reactions $\text{CH}_4 \longrightarrow \text{CH}_4^+, \text{CH}_3^+, \text{CH}_2^+, \text{CH}^+, \text{C}^+$ and $\text{H}^\cdot$

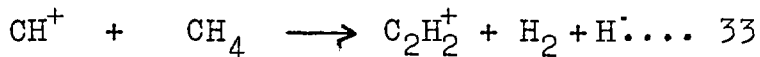
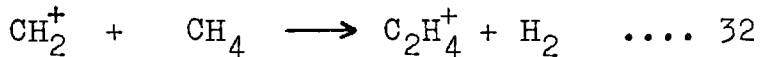
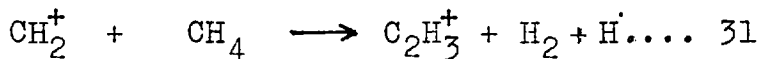
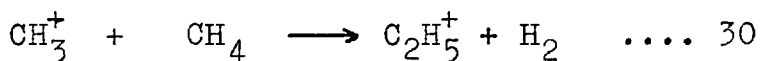
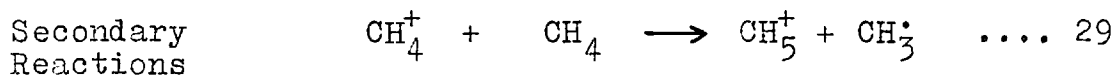
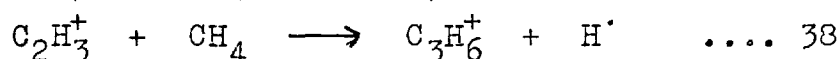
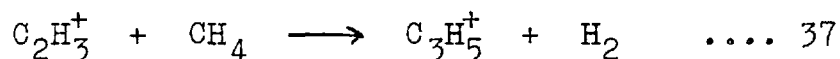
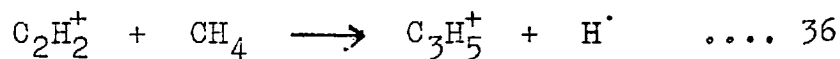
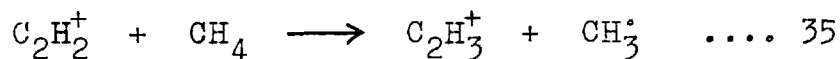
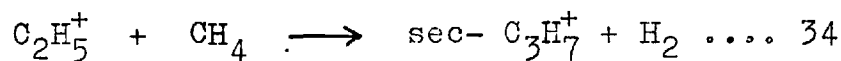
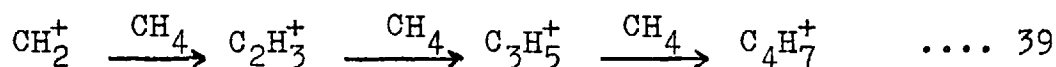


Table 1.Methane Mass Spectra at Various Pressures 10^{-4} to 1.9 mm Hg.

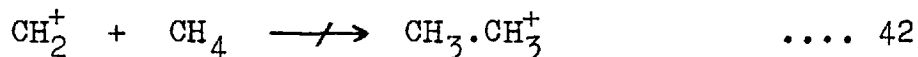
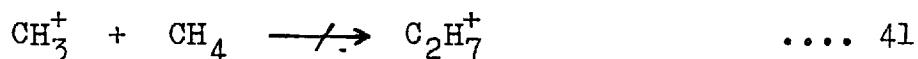
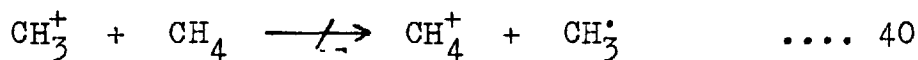
Pressure	10^{-4}	0.34	0.91	1.9
Ion.				
C^+	0.13	7.7×10^{-5}	-	-
CH^+	0.038	2.2×10^{-4}	4.1×10^{-5}	-
CH_2^+	0.076	7.7×10^{-4}	1.3×10^{-4}	-
CH_3^+	0.4	0.0061	8.3×10^{-4}	-
CH_4^+	0.47	0.004	6.0×10^{-4}	-
CH_5^+	0.005	0.351	0.478	0.452
$C_2H_2^+$	-	4.7×10^{-4}	-	-
$C_2H_3^+$		0.039	0.0051	5.3×10^{-4}
$C_2H_4^+$		0.032	0.02	0.024
$C_2H_5^+$		0.44	0.406	0.349
$C_2H_7^+$		8.5×10^{-4}	0.0012	0.0055
$C_3H_3^+$		0.0016	5.8×10^{-4}	3.6×10^{-4}
$C_3H_4^+$		0.0029	0.0016	0.0011
$C_3H_5^+$		0.086	0.055	0.053
$C_3H_7^+$		0.0047	0.0071	0.028
$C_4H_7^+$		6.3×10^{-4}	7.0×10^{-4}	0.0018
$C_4H_9^+$		5.5×10^{-4}	0.0013	0.0051
$C_5H_9^+$		0.7×10^{-4}	0.4×10^{-4}	0.0011
$C_5H_{11}^+$		0.6×10^{-4}	0.5×10^{-4}	

Tertiary
Reactions

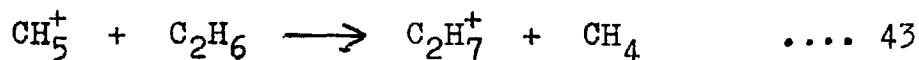
The reactions of the fragment hydrogen-deficient ions CH_2^+ , CH^+ and C^+ with methane, were found to be very fast (15), as had been surmised by Sieck and Johnsen (16). The reaction sequence for CH_2^+ may be written as:-



Several reactions which had been proposed were not observed to occur in the mass spectrometer.



Recent studies (using a tandem mass spectrometer) where methane was bombarded with methyl ions, showed that $C_2H_7^+$ could be formed (17). The $C_2H_7^+$ observed in methane was considered to be formed from ethane present as an impurity, by a ^{proton} ~~hydride~~ transfer reaction.



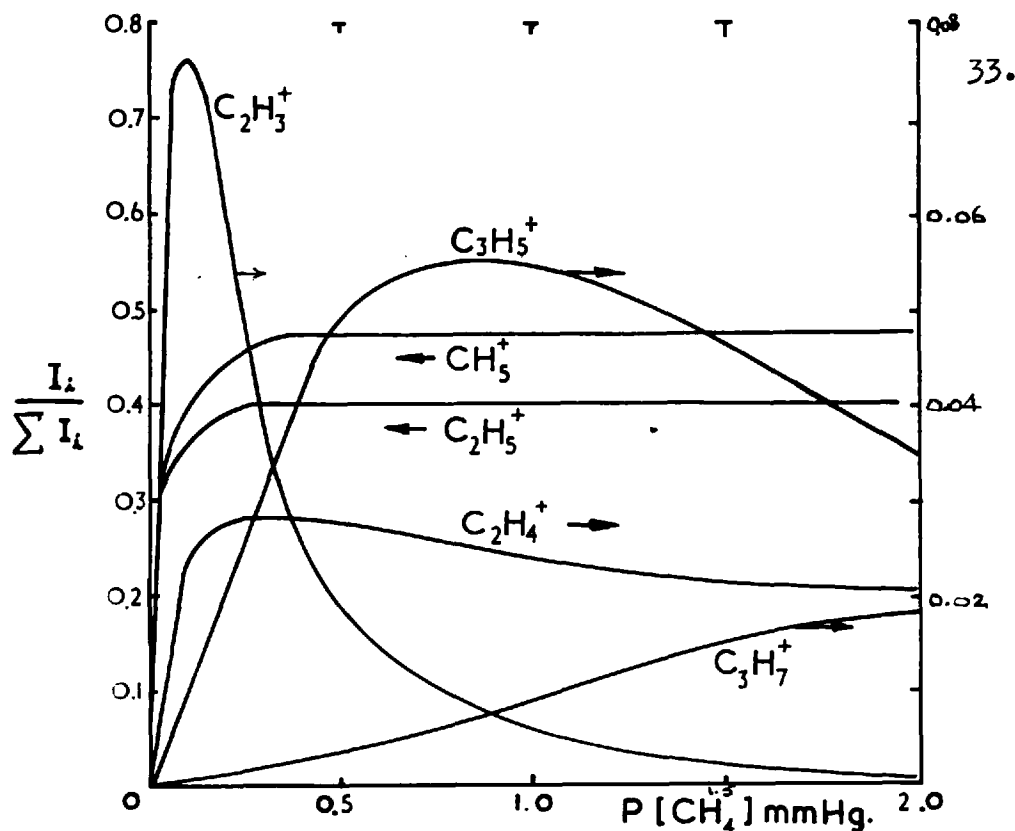


Fig.2. Relative concentrations of the major ions formed from methane in the mass spectrometer, against ionisation chamber pressure of methane.

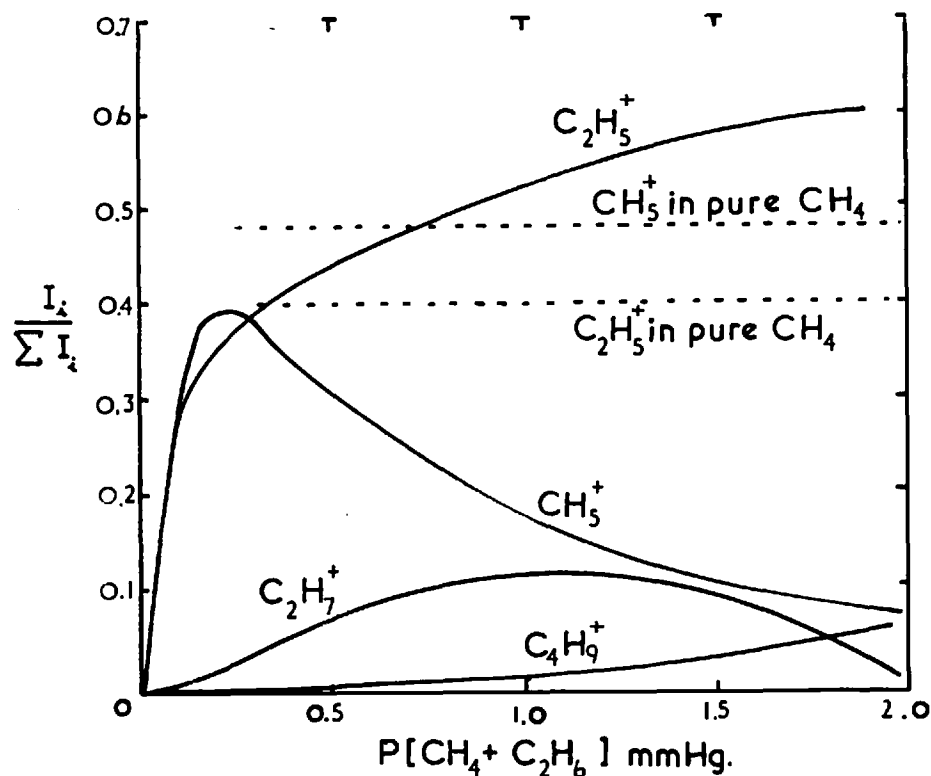
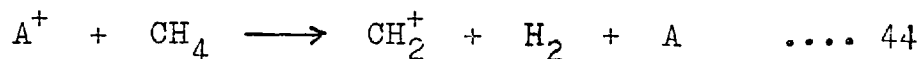


Fig.3. Relative concentrations of the major ions against total pressure of $\text{CH}_4 + 1\% \text{C}_2\text{H}_6$ in the source chamber.

The same authors, using deuterated compounds, demonstrated that the charge transfer reaction $\text{CH}_3^+ + \text{CH}_4 \rightarrow \text{CH}_4^+ + \text{CH}_3^\bullet$ does not occur. In the reaction of the methyl ion with methane, the sum of the product ions containing one carbon atom, was found to be about 5% of the total products containing two carbon atoms.

In the absence of higher hydrocarbons the concentrations of C_2H_5^+ and CH_5^+ reach a constant value, Fig. 2 page 33, indicating that further reaction with methane is slow. Experiments by Lampe (18) showed that ethane and propane from methane were formed simultaneously, and that propane did not arise from the irradiation of the ethane product. Lampe stated that provided the rate of reaction of CH_4^+ and CH_3^+ with methane was faster than the rate of their neutralisation, then the reaction between these ions and methane would account for the simultaneous build-up of higher hydrocarbons.

Reactions of CH_3^+ and CH_4^+ with methane were found to be very fast. The addition of higher hydrocarbons (about 1%) had no effect on the rate of formation of CH_5^+ and C_2H_5^+ , reactions 29 and 30 (15). The rapid build-up of products from CH_2^+ and CH^+ was confirmed, and the addition of argon was found to increase the rate of methane consumption, via the formation of CH_2^+ ions by charge transfer (20, 21).



Recent experiments by Cacace et al. (22), in which tritiated methane was allowed to decay in pure methane at 1 atmosphere, show that the distribution of ions obtained at 760 mm Hg is similar to that obtained in a mass spectrometer at low pressures using 70 eV electrons.

Reactions of the primary and secondary ions from methane with higher hydrocarbons were studied in a mass spectrometer (15). The ion distribution in the presence of 1% ethane and 1% propane, obtained by Munson is reproduced in Figs 3 and 4, p.p 33,36. The change in concentration of the ions was followed with increasing pressure in the source chamber, and the rates of reactions of the ions with various compounds were obtained (Table 2 page 37). The rate constants for the reactions of CH_5^+ and C_2H_5^+ with propane are of the order of 10^{-10} cc/molecule.sec. Similar values were obtained for reactions of these ions with butane, indicating that the reactions are very rapid.

Quantitative measurements of the yields of the various primary and secondary ions produced in the radiolysis of methane, were carried out by Ausloos et al. (24, 25, 26). Mixtures of deuterated plus non-deuterated reactants and additives, in the presence and absence of radical scavengers, were irradiated. The isotopic distribution of the products obtained was measured by mass spectrometric analysis. The reactions known to

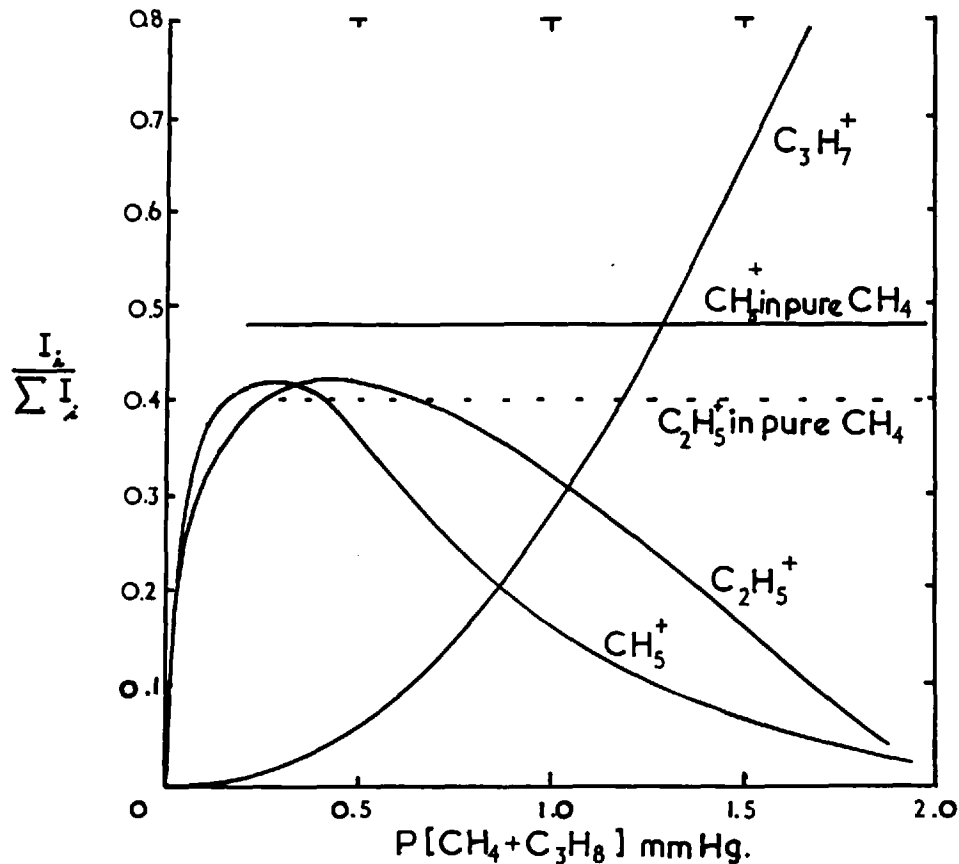


Fig. 4. Relative concentration of methyl, ethyl, and propyl ions against total pressure of $\text{CH}_4 + 1\% \text{C}_3\text{H}_8$.

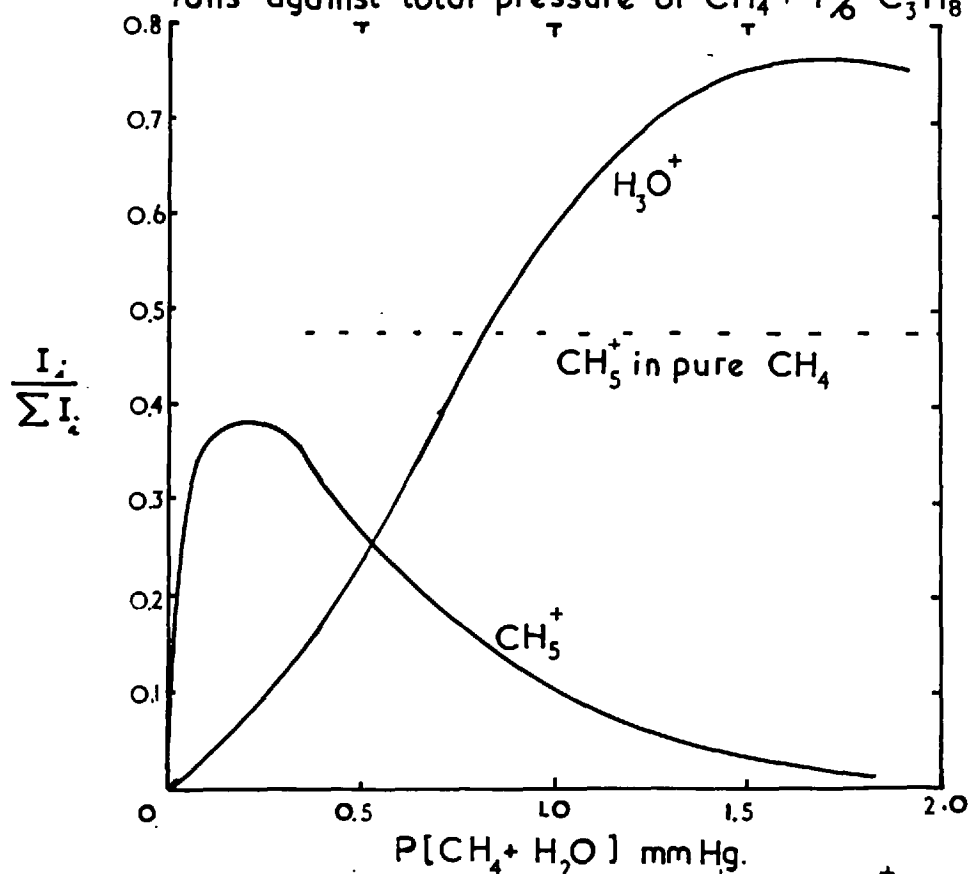


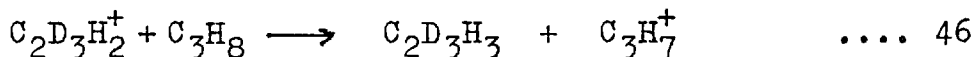
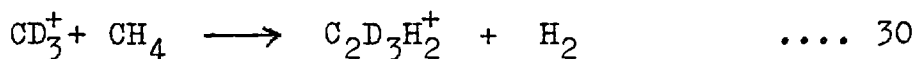
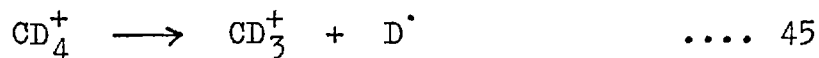
Fig. 5. Relative concentration of CH_5^+ and H_3O^+ against total pressure of $\text{CH}_4 + 1\% \text{H}_2\text{O}$.

Table 2.

Rates of Reaction of Ions with Various Compounds

Ion	Compound	k cc/molecule.sec.	REF
CH^+	CH_4	10^{-9}	19
CH_2^+	CH_4	10^{-9}	19
CH_3^+	CH_4	10^{-8} to 10^{-9}	19
CH_4^+	CH_4	10^{-8} to 10^{-9}	19
CH_5^+	CH_4	10^{-12}	15
CH_5^+	C_2H_6	6 x 10^{-9}	19
CH_5^+	C_3H_8	$\sim 10^{-9}$	19
CH_5^+	C_4H_{10}	-	-
C_2H_5^+	CH_4	10^{-12}	15
C_2H_5^+	C_2H_6	10^{-10}	19
C_2H_5^+	C_3H_8	6 x 10^{-10}	26
C_2H_4^+	CH_4	3 x 10^{-12}	15
C_2H_3^+	CH_4	0.9 x 10^{-10}	15
C_2H_2^+	CH_4	4.6 x 10^{-10}	15
C_3H_5^+	CH_4	small	15
O_2^+	CH_4	4 x 10^{-11}	26
CH_5^+	O_2	5 x 10^{-11}	26
C_2H_5^+	O_2	2 x 10^{-11}	26
CH_5^+	NO	5 x 10^{-11}	26
C_2H_5^+	NO	1 x 10^{-11}	26
CH_5^+	H_2O	10^{-8}	26
C_2H_5^+	H_2O	6 x 10^{-9}	26

occur in the mass spectrometer were confirmed from the isotopic forms of the products. For example irradiating CH_4 plus CD_4 in the presence of nitric oxide showed methyl and ethyl ions to be present.



Results obtained from experimental observations, and by calculation from the cracking pattern of methane using 70 eV electrons, are given in Table 3.

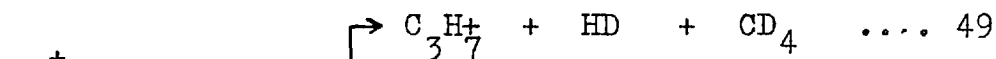
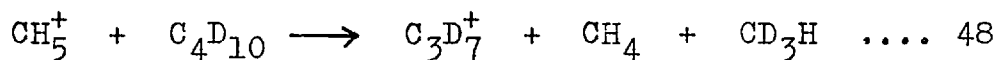
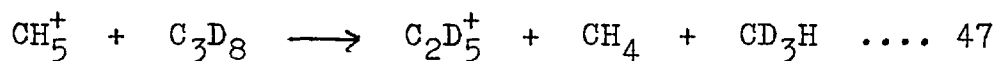
Table 3.

G-values of some Primary and Secondary ions in Methane.

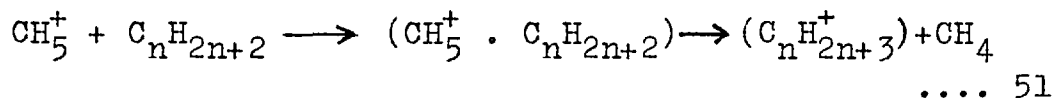
Ion	G-value			
	Calculated	Ref	Experimental	Ref.
CH_4^+	1.5 to 1.7	(16)		
CH_3^+	1.5	(16)		
CH_2^+	0.2 to 0.3	(16)		
CH^+	0.14	(16)		
C^+	0.04	(16)		
CH_5^+			1.9 ± 0.2	(24)
C_2H_5^+			0.9 ± 0.2	(24)
C_3H_7^+			≥ 0.06	(23)

It can be seen from the above Table 3 that the major primary ions react with methane to give nearly quantitative yields of CH_5^+ and C_2H_5^+ .

Further reactions of CH_5^+ and C_2H_5^+ which were shown to occur using deuterated hydrocarbons as additives are:-



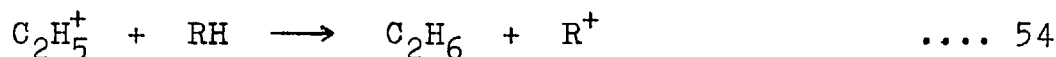
The reaction of CH_5^+ with $\text{C}_n\text{H}_{2n+2}$ gives rise to an unstable ion-molecule, which then fragments (15). These reactions may be written in general terms as:-



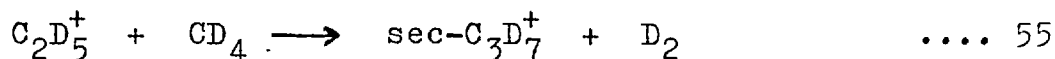
The mode of decomposition of $\text{C}_n\text{H}_{2n+3}^+$ should depend upon the energy with which it was formed.



The main reaction of the ethyl ion is the hydride ion transfer reaction,



Reaction 55 does not occur to any great extent since $G(\text{sec-C}_3\text{H}_7^+)$ was found to be about 0.06 (23).



In the presence of the higher hydrocarbons the formation of ethane by reaction 54 is rapid, and accounts

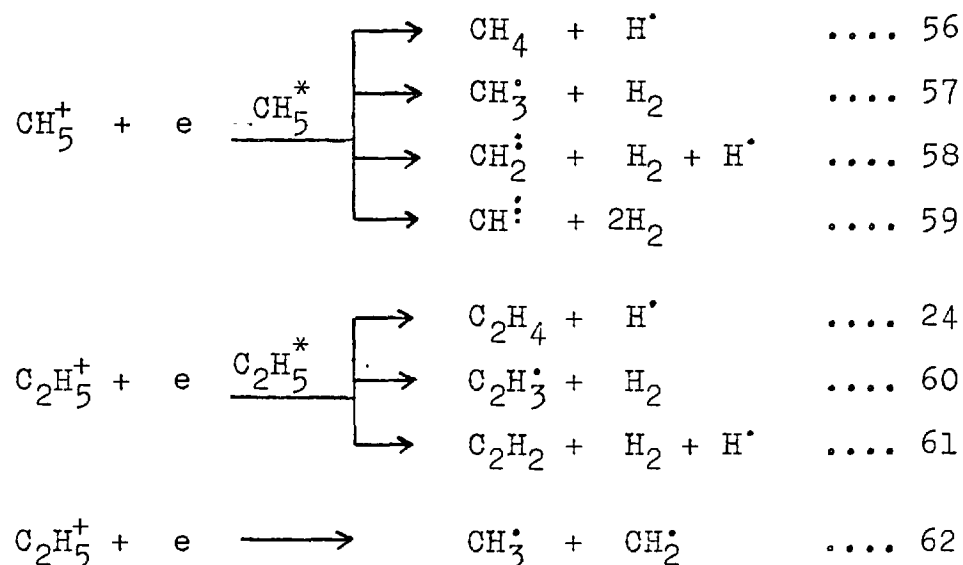
for a large part of the ethane yield.

The effect of the kinetic energy of various ions on the products formed was studied by Abramson and Futrell (17). Using a tandem mass spectrometer arrangement, an ion was selected in the first mass spectrometer and injected into the second, which contained the gas to be bombarded. The product ions formed were found to depend upon the translational energy of the impinging ion.

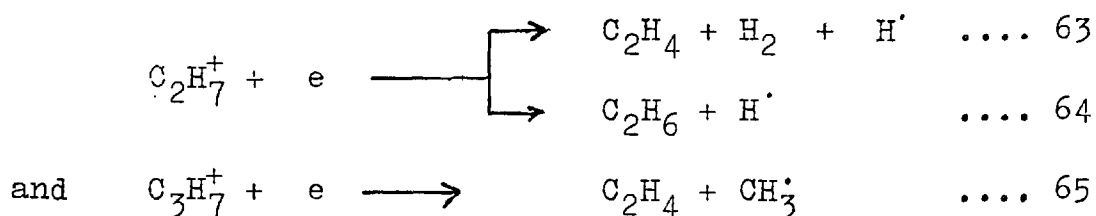
In the absence of hydrocarbon scavengers the CH_5^+ and C_2H_5^+ ions have been found to be unreactive in pure methane. Even where the level of hydrocarbon impurities in methane is of the order of 0.002% the ethyl ions will undergo hydride transfer reactions to yield ethane (24).

In the presence of 1% of the radical scavenger oxygen, or nitric oxide, the distribution of hydrocarbon ions was observed to be essentially the same as for methane in the mass spectrometer at 2 mm Hg pressure (12). The major product ions CH_5^+ , C_2H_5^+ , C_2H_4^+ , C_3H_5^+ , and C_3H_7^+ do not therefore react rapidly with oxygen or nitric oxide. This is at variance with the conclusion reached by Ausloos et al. (24). They observed a decrease in the product yields when oxygen or nitric oxide was added to methane plus propane (90% CH_4 , $\text{O}_2/\text{C}_3\text{H}_8 = 10$) prior to irradiation. These effects were attributed to reactions of CH_5^+ and C_2H_5^+ with oxygen or nitric oxide.

The disagreement is however a question of magnitude only, since the reaction between the ions and oxygen does occur, but only slowly (27). Where the relative concentration of oxygen to hydrocarbon -ion scavenger was larger than about 20, both authors agree that a reduction in product yields would be expected. The inference is that in the presence of oxygen plus higher hydrocarbons ethyl ions are not neutralised. Because in the radiolysis of pure methane, the rate of reaction of the CH_5^+ and C_2H_5^+ ions with methane has been shown to be slow (27), neutralisation of these ions was proposed (20, 28, 29).



Other ions which have been considered to be neutralised are (7, 8, 20) :-



Neutralisation of an ion would be expected to give rise to a neutral excited species which could be deactivated by collision or decompose to yield radicals and neutral fragments. All of the above neutralisation reactions for CH_5^+ and C_2H_5^+ are stated to be energetically possible (28). In the radiolysis of methane plus oxygen (22), some neutralisation of the ethyl ion was observed, with the subsequent formation of ethylene. The yield was stated to be about one fifth of that had all the ethyl ions been neutralised to yield ethylene. (From Table 3 page 38 $G(\text{C}_2\text{H}_4)$ would be about 0.2 on this basis). The formation of ethylene by the neutralisation of C_2H_5^+ , and C_2H_7^+ and C_3H_7^+ was proposed by Hummel and Meisels respectively (20, 7, 8).

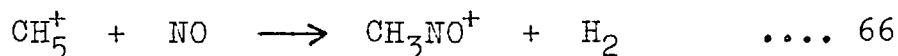
The formation of a methyl and a methylene radical on the neutralisation of C_2H_5^+ , reaction 62, was postulated by Pratt and Wolfgang (66). Cacace et al. also considered this reaction to be feasible (22).

Evidence against the neutralisation of the ethyl ion yielding ethylene was put forward by Ausloos (24). The yield of ethylene C_2D_4 , from the radiolysis of $\text{CD}_4 + 0.5\% \text{C}_3\text{H}_8 + 6\% \text{NO}$ remained unaffected under conditions where the ethyl_{radical} was scavenged (by the large amount of nitric oxide present). It was thus concluded that most of the ethylene in the radiolysis of methane or methane plus nitric oxide was probably not related to the ethyl ion.

However, propane was present as well as nitric oxide, and is also an ion scavenger. Propane probably reacts much faster with $C_2H_5^+$ than does nitric oxide; sufficiently fast in fact to remove some of the ethyl ion even though the ratio of nitric oxide to propane is about 12. Also, the rate of reaction between nitric oxide and $C_2H_5^+$ has not accurately been determined and no firm conclusions can yet be drawn.

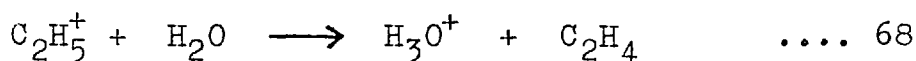
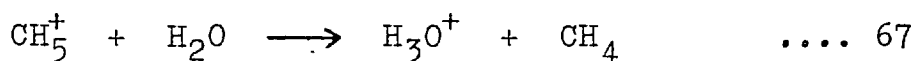
Using a mass spectrometer, reactions of ions with various compounds have been studied (26, 27). In the mass spectrometer, reactions of the secondary ions CH_5^+ and $C_2H_5^+$ with oxygen have been observed to be slow. Yet, in the radiolysis of methane plus oxygen and propane, the yield of ethane was depressed when the ratio of oxygen to propane was high (24). Similarly when nitric oxide was used as a scavenger, the ethane yield decreased. At the same time, the yield of hydrogen increased as the scavenger/propane ratio was increased.

To account for these observations a reaction between the scavenger and the ion CH_5^+ was proposed.



There would appear possibly to be some difference between the scavenging mechanism of oxygen and nitric oxide. The yield of ethane for the same scavenger/propane ratio is higher in the case of oxygen, than for nitric oxide (24).

The ions CH_5^+ and C_2H_5^+ were found to be readily scavenged by water (26). The secondary ion distribution from methane in the presence of 1% water was obtained by Munson and Field and is reproduced in Fig.5 page 36 (26). Reactions 67 and 68 were put forward to account for the disappearance of the two ions.



Ammonia was similarly shown very effectively to scavenge the secondary ions, with the proposed formation of methane and ethylene as above.

The rate constants for reactions 67 and 68 were estimated to be of the order of 10^{-8} and 6×10^{-9} cc/molecule. sec. respectively. The ions C_2H_4^+ and C_3H_5^+ were observed to be unreactive towards water.

Although the presence of positive ions has been confirmed and thoroughly investigated, the existence of negative ions (other than electrons) and their reactions have not been widely dealt with. Only one paper was found with any bearing on the matter with respect to methane (30). The concentration and distribution of the negative ions present in methane was studied in a mass spectrometer at a pressure of 10^{-5} mm Hg. The ions C^- , CH^- , CH_2^- , and CH_4^- were noted, the percentage of each being 47.2, 40.4, 12 and 0.4 respectively. Results

indicated that positive ions were present in very much greater numbers than the negative ions.

The formation of a polymer as a result of irradiating methane was noted by Lind (6), who suggested that it arose from reactions of unsaturated hydrocarbons. The empirical formula of the long chain molecule is generally agreed to be C_nH_{2n} (6, 7, 8, 16, 18, 31, 32). The number of carbon atoms found per molecule varied between 6 and 22 (16, 18, 32), indicating that the polymer was of extremely diverse composition. Infra-red (31) and nuclear-magnetic resonance (16) spectra of the polymeric material showed that the ratio of methyl to methylene groups in the molecule was between 1.6 to 2.0. A G-value of formation of 0.016 was obtained by Davis from methane irradiated at 77°K. The yield was not affected by the presence of air, xenon, nitric oxide, or carbon tetrachloride (32).

The rate of polymer formation in pure methane was found to increase on adding ethylene prior to irradiation, suggesting that the formation of the polymer may involve ethylene formed in the radiolysis (16). The addition of nitric oxide to methane prior to irradiation was observed to have no effect on the rate of polymer formation. Although the addition of ethylene increased the rate of polymer formation, in methane plus nitric oxide the ethylene yield was high compared with that from pure methane, yet the rate of polymer production was not

altered by the addition of nitric oxide. A free radical scheme leading to polymer formation is therefore considered unlikely. G (polymer), in terms of methane consumed to form the polymer, was 2 in the presence of nitric oxide. Consecutive ion-molecule reactions involving the hydrogen-deficient fragment ions CH^+ and C^+ were proposed as a mechanism by which the polymer could be formed (15, 16). Since reactions of these ions with ethylene are possibly quite fast, ethylene could play a part in polymer formation when the ethylene concentration is sufficiently high.

If the polymer arises from reactions of CH^+ and C^+ with methane, then $G(\text{polymer})$ should equal that of $G(\text{CH}^+ + \text{C}^+)$ which is about 0.2 (Table 3 page 38). If CH_2^+ also contributes to polymer formation then the G -value will increase to about 0.4 to 0.5 (Table 3 page 38). Davis (32) agrees with this mechanism, but he obtained a much lower G -value. If the average number of carbon atoms per polymer molecule is about 10, the $G(\text{polymer})$ from Sieck and Johnson's results is about 0.2.

Mass spectrometer studies, and experiments involving the use of deuterated compounds have conclusively demonstrated the presence of ions and the occurrence of ion-molecule reactions in methane radiolysis. The primary ions CH_4^+ , CH_3^+ , CH_2^+ , CH^+ and C^+ all react rapidly with methane.

G-values for the formation of CH_5^+ , C_2H_5^+ , and C_3H_7^+ in methane radiolysis, of 1.9 ± 0.2 , 0.9 ± 0.2 and about 0.06 respectively have been obtained experimentally. These values for CH_5^+ and C_2H_5^+ compare well with the values for $G(\text{CH}_4^+)$ and $G(\text{CH}_3^+)$ $[G(\text{CH}_4^+ + \text{CH}_3^+) = 3]$ which have been calculated from the 70 eV cracking pattern of methane, assuming that CH_4^+ and CH_3^+ give rise to CH_5^+ and C_2H_5^+ respectively. The small discrepancy is probably due to the formation of $\text{sec-C}_3\text{H}_7^+$ from C_2H_5^+ and methane.

Reactions of CH_5^+ and C_2H_5^+ with methane are slow, and there is some evidence that they may be neutralised to yield a number radicals and molecules. In methane plus oxygen or nitric oxide evidence against their being neutralised is well founded, but what these ions give on reaction with oxygen or nitric oxide is unknown.

In the presence of higher hydrocarbons the CH_5^+ and C_2H_5^+ react rapidly with the additive, by ion-molecule complex formation for CH_5^+ , and hydride ion transfer for C_2H_5^+ . The ion-molecule complex decomposes to give a smaller ion and neutral fragments. Evidence for reactions of CH_5^+ and C_2H_5^+ with oxygen and nitric oxide has been obtained experimentally, mass spectrometer studies indicating that the reactions are slow.

The hydrogen-deficient ions CH_2^+ , CH^+ , and C^+ rapidly react with methane probably giving rise to a chain reaction, the product being a high molecular weight compound having about 10 to 15 atoms per molecule.

Section 2. Radiation Chemistry of Methane plus Oxygen; Oxygenated Product Formation.

Section 2.1 Radical Mechanisms.

The ability of high energy radiation to bring about oxidation was early recognised (6, 42, 43). More recently, practical interest in radiolytic oxidation has been stimulated by the oil companies, and academic interest by the desire to extend the knowledge of combustion chemistry. In general, radiation may promote thermal oxidation reactions by initiating chain reactions at lower temperatures than those normally required.

The decomposition of the hydrocarbons by radiation yields radicals, which then react with the oxygen present. To determine the mechanism by which products are formed, the product yields must be measured at low radiation doses, so as to minimise the secondary decomposition by radical attack and radiolytic degradation.

The radiolysis of methane plus oxygen mixtures using alpha particles was carried out in 1926 by Lind (6). The oxidation was taken to completion, carbon dioxide and water being the end products. The G-value for the disappearance of methane was found to vary from about 12 to 14 (based on $W = 29$), in the presence of excess oxygen or methane respectively.

The partial radiolytic oxidation of methane was investigated by Mikhailov et al (44). Irradiations were performed with 90 to 120 keV electrons at a dose-rate of

2.7×10^{16} eV/ml/sec. The product yields obtained at a dose of 5×10^{19} eV/ml are given in Table 4.

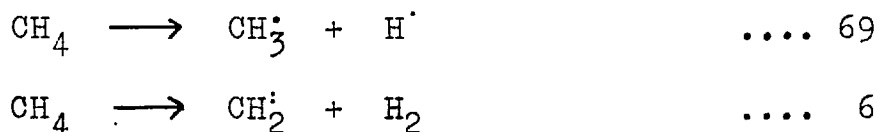
Table 4.

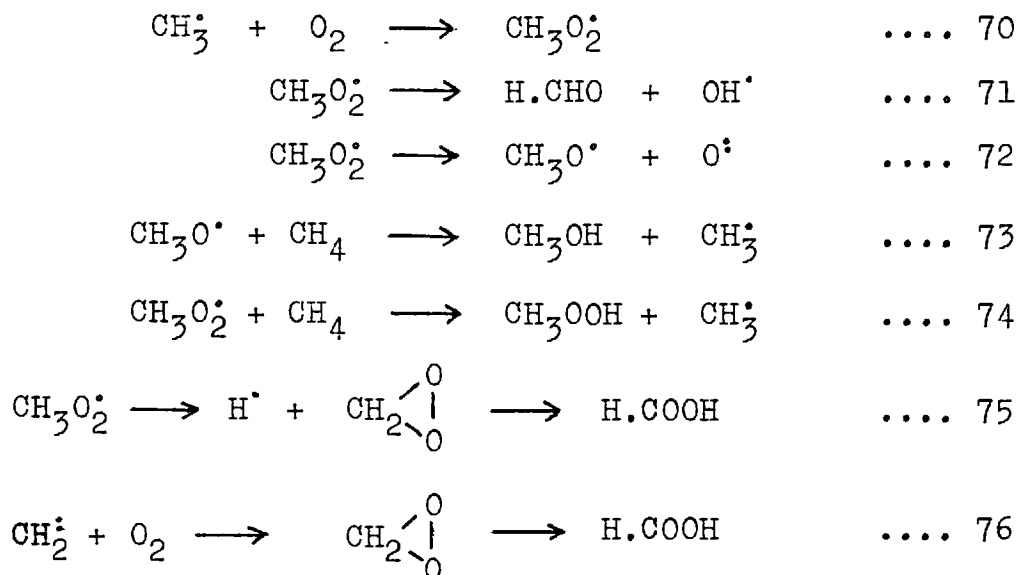
G-values for Product Formation from the Radiolytic Oxidation of Methane using High Energy Electrons.

Product	G-value
CO	1.2
CO ₂	1.8
H ₂	3.7
H.CHO	0.3
Peroxides	0.3
CH ₃ OH	0.35
H.COOH	2.5

The low product yield, which was found not to alter much over the temperature range -80 to 160°C , indicated the absence of chain processes. In view of the large doses used, the G-values obtained are not considered to be representative of the initial product yields. A surface effect was noted, a brass vessel giving the fastest rate and most extensively oxidised products. Using a pyrex vessel, a higher yield of formaldehyde was obtained.

The following reaction scheme was proposed to explain the formation of the products.

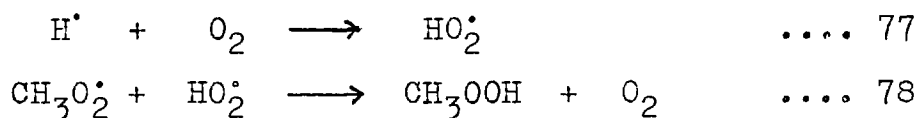




Reactions 73 and 74 would give rise to a chain reaction, and are most unlikely to occur at both of the temperature extremes considered. Similarly reactions 72, 75, and 76, must be considered to be purely speculative, and in general not in accord with recent evidence.

An analysis of the peroxide products from the radiolysis of methane plus oxygen using cobalt 60 gamma radiation (45) showed that methyl hydroperoxide was the only constituent present. The yield was independent of the concentration of oxygen over the range 0.1 to 10 mole % oxygen. At room temperature, and at a dose-rate of 3×10^{12} eV/ml/sec, $G(\text{CH}_3\text{OOH})$ was found to be 3.5, and was independent of the dose received up to 4×10^{16} eV/ml.

The methyl hydroperoxide was considered to be formed by the abstraction of hydrogen from the hydroperoxy radical $\text{HO}_2\dot{\text{C}}$ by methyl peroxy radicals.



An extensive study of the products from the radiolysis of methane plus 10% oxygen using 4 MeV electrons, and cobalt 60 gamma radiation, was carried out by Hearne and Hummel (46, 47). The effects of pressure, dose-rate and dose, on the initial product yields were investigated. The yield of methyl hydroperoxide was found to increase with increasing dose-rate, and increasing pressure at a given dose-rate. The formaldehyde yield was about half that of the methyl hydroperoxide and behaved similarly with respect to dose-rate and pressure. The G-values obtained for the major products are given in Table 5.

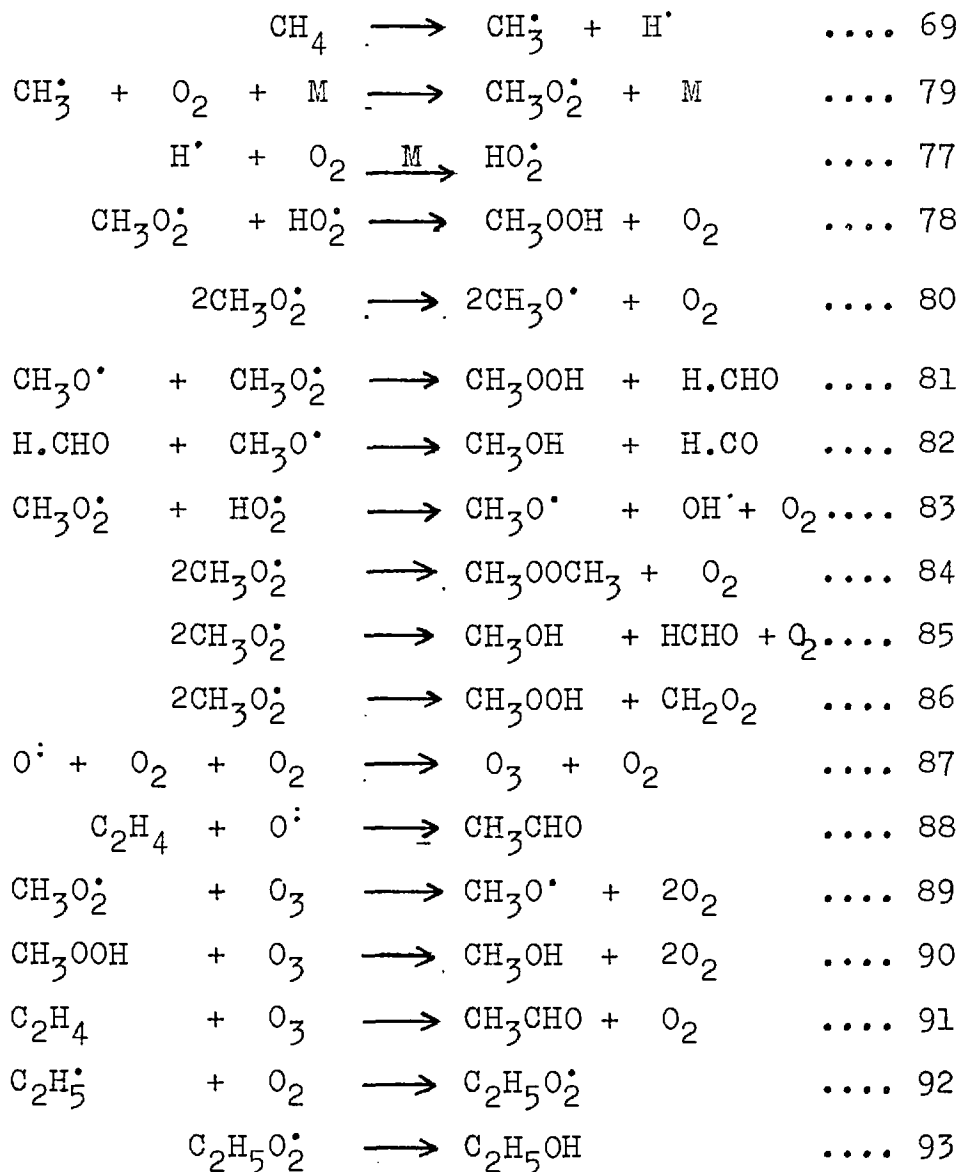
Table 5.

G-values for the Major Products from the Radiolysis of Methane plus 10% Oxygen, using 4MeV Electrons and Co⁶⁰ Gamma Radiation.

Product	4 MeV Electrons 72 cm Pressure.	Dose- rate	Co ⁶⁰ Gamma 76 cm Pressure.	Dose- rate
CH ₃ OOH	5.99	9.62x10 ¹⁷ eV/ml/ min.	2.0	3.12x10 ¹⁴ eV/ml/ min.
H.CHO	2.4	"	1.25	"
CH ₃ OH	1.6	5.38x10 ¹⁷ "	1.6	2.4x10 ¹⁴ "
C ₂ H ₅ OH	0.607	"	0.23	"
C ₂ H ₄	0.44	"	0.44	"
C ₂ H ₆	0.155	"	0.146	"
CH ₃ CHO	0.075	"	0.075	"

The formation of the products was based entirely on

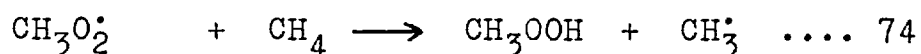
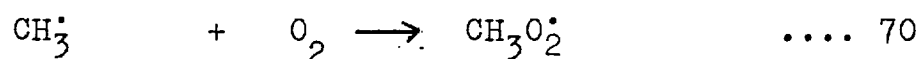
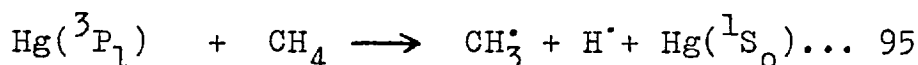
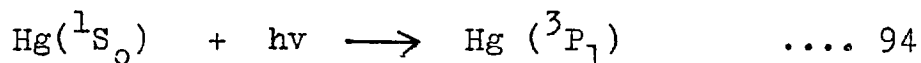
reactions of the various radicals and atoms produced in the system by the radiation. The species formed may react with the reactants, radicals, or other intermediates present. No firm mechanism was proposed, but the following reactions were considered to be important in product formation.



Methanol was stated to be the major oxygenated product

obtained from the radiolysis of methane plus oxygen, using fission fragments (48). The methane conversion was about 10%, no other details are available.

The mercury photosensitised oxidation of methane at 25°C using a flow system was carried out by Gray (49). High rates of flow were maintained to prevent the decomposition of the peroxide products due to thermal or photochemical action. The main product formed was methyl hydroperoxide, very little formaldehyde being noted and no analyses were performed to determine whether methanol was present. The mechanism proposed for product formation was:



It was stated that decomposition of the peroxide by mercury vapour could give rise to the small amounts of formaldehyde observed. The formation of the peroxide is more likely to occur by reaction 78 rather than by hydrogen abstraction from methane. As will be seen later, for hydrogen abstraction to occur, the dissociation bond energy has to be less than about 70 kcal/mole, and this is definitely not the case in methane $D(\text{CH}_3\text{-H}) \approx 100$ kcal/mole.

Few G-values for the disappearance of oxygen during radiolysis have been reported in the literature. In the

radiolytic oxidation of methane (Mikhailov 44) to very large conversions, the ratio of oxygen to methane consumed was found to be 7 to 6. Based on Lind's values for methane consumed (page 48), G_{-O_2} is approximately 15.

Determinations of $G(-O_2)$ in methane plus various concentrations of oxygen, were performed by Riley and Hung (50). $G(-O_2)$ was found to increase with increasing oxygen concentration. At a concentration of 370 p.p.m. of oxygen, $G(-O_2)$ was 13.3.

From the oxygen appearing in the products of the radiolytic oxidation of methane, whose yields have been measured, minimum values for $G(-O_2)$ can be calculated.

Table 6.

$G(-O_2)$ based on the Oxygen found in the Products from the Radiolytic Oxidation of Methane.

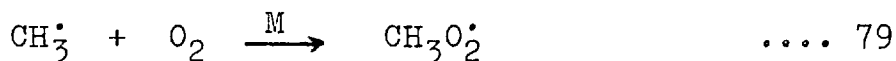
$G(-O_2)$	Dose-rate eV/ml/min	Reference
7.1	10^{18}	Mikhailov,
8.7	10^{18}	Hearne & Hummel,
3.8	3.8×10^{14}	" "
13.3	-	Riley & Hung.

Since not all of the product yields have been measured, the above calculated figures must be minimum values.

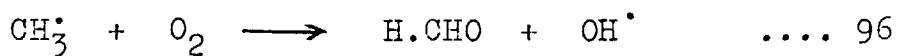
Reactions between methyl radicals and oxygen are important in the radiolytic oxidation of methane. The reactions have been extensively investigated in the photo-

oxidation of many compounds, which give rise to methyl radicals on photolysis (51).

The order of the reaction is open to question as evidence for both second order and third order processes exists (52, 53, 54, 55). Recent experimental results obtained from the photo-oxidation of azo-methane (56) confirmed that the first step in the reaction between methyl radicals and oxygen was the formation of the methyl peroxy radical, probably by a third order process.



This reaction probably occurred over the whole range of pressures studied, from about 1 mm Hg to 760 mm Hg. From the second order reaction postulated (52, 53, 54), the products are formed directly, and not via the methyl peroxy radical.

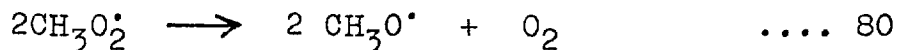


Evidence for this reaction was obtained from the photo-oxidation of methyl iodide (57). The addition of deuterium iodide gave rise to DOH, showing that hydroxyl radicals were present. However, results obtained by Gray (49) from the mercury sensitised oxidation of methane at 25°C, definitely exclude the possibility of reaction 96, as no formaldehyde was found as a product.

Reactions of the methyl peroxy radical in the absence of hydrogen atom donors account for the products observed

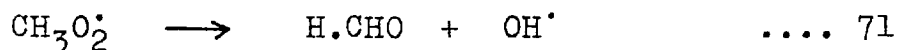
in systems containing methyl radicals and oxygen.

In the photo-oxidation of methyl iodide, Heicklen and Johnston found that the major radicals present were $\text{CH}_3\dot{\text{C}}\text{H}_2$, $\text{CH}_3\text{O}\cdot$, and $\text{CH}_3\text{O}_2\cdot$. The most important radical was $\text{CH}_3\text{O}\cdot$ which was considered to arise from methyl peroxy radicals (55).

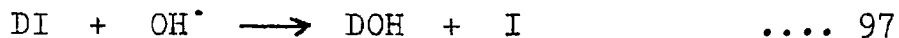


The presence of alkoxy radicals was also noted by Dever and Calvert (58), and Farren et al. (59), who considered that the relative concentration of $\text{CH}_3\text{O}\cdot$ was smaller than did other workers.

In the absence of readily abstractable hydrogen, reaction 80 is generally agreed to be the major reaction of the methyl peroxy radicals. Some decomposition of $\text{CH}_3\text{O}_2\cdot$ to yield formaldehyde may occur.

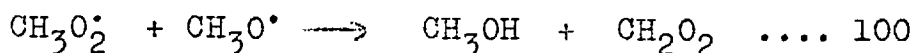
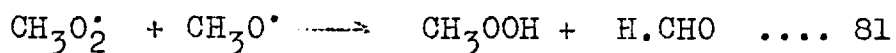
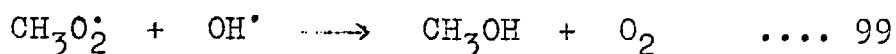
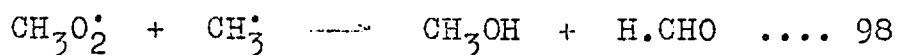


The presence of DOH when deuterium iodide was added to $\text{CH}_3\text{I} + \text{O}_2$ mixtures prior to photolysis, was given as evidence for this reaction. The iodide yields water by scavenging the hydroxyl radicals.



This reaction was also given as evidence for the occurrence of the second order reaction between methyl radicals and oxygen (reaction 96). It would not be possible to determine whether reaction 71 occurred to a limited extent, or reaction 96 proceeded only to a limited extent. Further

reactions involving the methyl peroxy radical which have been proposed are:



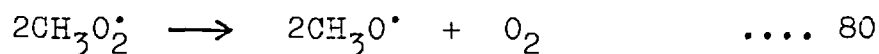
Reaction 98 is unlikely to be important in oxygen-rich systems. Since the rate of reaction of methyl radicals with oxygen is very fast, there are not going to be any free methyl radicals.

Barber et al. (57) considered methanol to be formed in the photolysis of methyl iodide plus oxygen and hydrogen iodide, by reaction 99. Heicklen (60) has shown from kinetic considerations that this reaction will not occur in systems where readily abstractable hydrogen is available, e.g. HI. In these systems, the methyl peroxy radical is rapidly scavenged by HI.

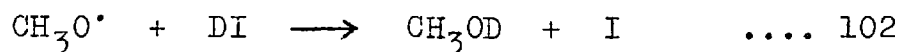
The formation of methyl hydroperoxide in systems containing excess oxygen was suggested by Subbaratnam and Calvert (61) to arise from the disproportionation reaction 81. The addition of formaldehyde to methyl iodide plus oxygen prior to photolysis caused a decrease in the methyl hydroperoxide yield. The aldehyde was considered to react with the methoxy group to give methanol thus decreasing the methyl hydroperoxide yield by removing $\text{CH}_3\text{O}^\bullet$, and hence substantiating the above reaction 81.

The reaction leading to methanol and CH_2O_2 was put forward by Dever and Calvert (58) for the formation of formic acid in the photo-oxidation of azo-methane. CH_2O_2 was thought to isomerise to formic acid, or to dissociate. The reaction is thermochemically feasible but has not been confirmed experimentally. The amount of formic acid observed as a product was stated to be small, and the reaction can thus only be of minor importance.

In the photo-oxidation of methyl iodide (57) and azo-methane (56, 58), methanol and formaldehyde were observed to be the main products, formed in approximately equal amounts. This observation has been explained on the basis of a disproportionation reaction of methoxy radicals.

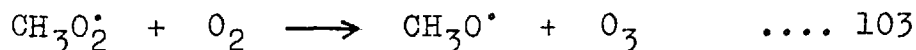


Heicklen (60) also considered this reaction 101 to be responsible for the formation of the observed products. However, Farren et al. (59) obtained little CH_3OD on adding DI to methyl iodide plus oxygen and then photolysing, and concluded that the concentration of the methoxy radicals was small.



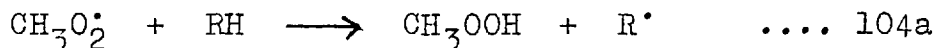
The formation of ozone by the reaction of oxygen with

methyl peroxy radicals was postulated by Hanst and Calvert (62) and other workers (58, 61).



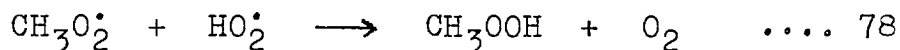
This reaction is about 25 k cal/mole endothermic and is therefore unlikely to occur at room temperature. The presence of ozone as a product, from the photolysis experiments, has not been established, the amount observed being of the order of the experimental error. The stationary state concentration of ozone would be expected to be very low, due to its reactivity.

In systems where the methyl peroxy radical can abstract hydrogen, methyl hydroperoxide is the major product (45, 49, 59).

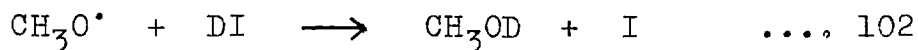


This reaction has been investigated for a number of possible hydrogen donors. The rate of formation of methyl hydroperoxide was not enhanced by the addition of acetaldehyde or deuterated formaldehyde, to systems containing methyl peroxy radicals. Both of these additives are good hydrogen donors. The addition of hydrogen bromide similarly did not lead to an increase in the peroxide yield (59). In the presence of hydrogen iodide or deuterium iodide, the rate of formation of CH_3OOH or CH_3OOD increased markedly, at the expense of the other products. It has been concluded that the

hydrogen abstraction by methyl peroxy radicals depends upon the bond dissociation energy of the hydrogen donor. Abstraction will only occur where the bond energy $D(R-H)$ is less than a certain value. $D(H-Br)$ and $D(H-I)$ are 86.4 kcal/mole and 70.4 kcal/mole respectively. Methyl peroxy radicals will abstract hydrogen from hydrogen iodide but not from hydrogen bromide. Hence the minimum value for the dissociation energy for abstraction to occur is about 70 to 75 kcal/mole. Since $D(H-O_2)$ is about 47 kcal/mole (63), methyl peroxy radicals will readily abstract hydrogen from the hydro peroxy radicals $HO_2^\bullet$.

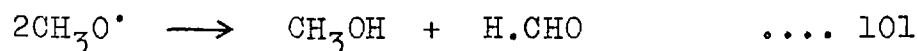


Deuterium abstraction from DI by the methoxy radical was thought, by Barber et al., to occur readily but was not confirmed (62).

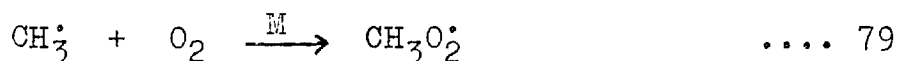


The mechanism proposed by Farren et al. (59) for methanol formation in the photo-oxidation of methyl iodide in the presence of hydrogen iodide, was queried by Heicklen (60). Hydrogen iodide scavenges the methyl peroxy radicals, and a reaction scheme for methanol from $CH_3O_2^\bullet$ is then difficult to envisage. In the presence of hydrogen bromide, which scavenges hydroxyl radicals, the reaction $CH_3O_2^\bullet + OH^\bullet \longrightarrow CH_3OH + O_2$ will not

occur, yet methanol was still found to be present as a product. Heicklen proposed that both of these observations (methanol formed in the presence of HI and HBr) can be explained if methanol is formed primarily from methoxy radicals. Since hydrogen bromide does not scavenge methoxy radicals, the products observed could be formed by reaction 101.



From the experimental data available at this moment, the conclusion is that at pressures about atmospheric, the reaction between methyl radicals and oxygen leads to the formation of methyl peroxy radicals.

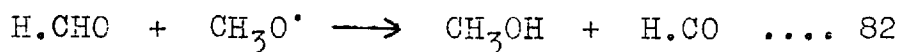


Where no source of abstractable hydrogen is available, the methyl peroxy radicals react to give methoxy radicals.

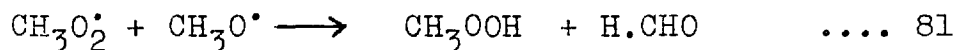
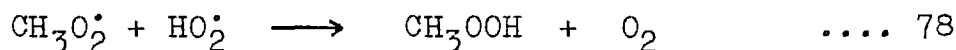


Other reactions of $\text{CH}_3\text{O}_2^\bullet$ with $\text{OH}^\bullet$, $\text{H}\cdot\text{CHO}$ and $\text{CH}_3\text{O}^\bullet$ groups may occur, depending upon the relative concentrations. Disproportionation of methoxy radicals yields methanol and formaldehyde, reaction 101.

The formaldehyde may react with methoxy radicals to give methanol.



Methyl hydroperoxide arises principally by hydrogen abstraction from HI or $\text{HO}_2^\bullet$ where these reactants are present. Some methyl hydroperoxide may be formed by reactions between $\text{CH}_3\text{O}_2^\bullet$ and $\text{CH}_3\text{O}^\bullet$.



Section 2.1.1 High Temperature Oxidation.

The partial oxidation of hydrocarbons at high temperatures (greater than 500°C) involves several steps in which radicals participate. Hydrogen abstraction reactions are important under these conditions. The major products are formaldehyde, carbon monoxide, carbon dioxide, and water, and the amounts of each product are dependent upon the conditions of oxidation. Surface effects have been found to have an effect on the product formation.

Gray (49) and Shannin and Kutsche (65) suggest that the methyl peroxy radical may well be stable at temperatures greater than 160°C , and that the thermal oxidation could proceed via this radical.

In general however no parallel can be drawn between thermal oxidation and the radiation-induced oxidation at room temperatures.

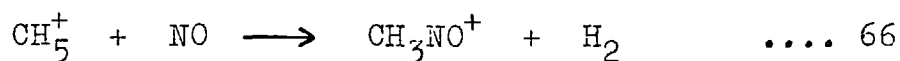
Section 2.2 Ionic Mechanisms.

The radiolytic, and photo-oxidation of hydrocarbons has been assumed to give rise to radicals. Reactions between the radical intermediates themselves, and with the reactants, have been postulated in mechanisms for the formation of the observed products. Until recently, reactions between ions and reactants to give products had not been considered (24, 26, 27, 51).

Oxygen, an efficient electron scavenger, would give rise to O_2^- and O^- . Neutralisation of these two species by positive alkyl ions could yield oxygenated compounds (51).

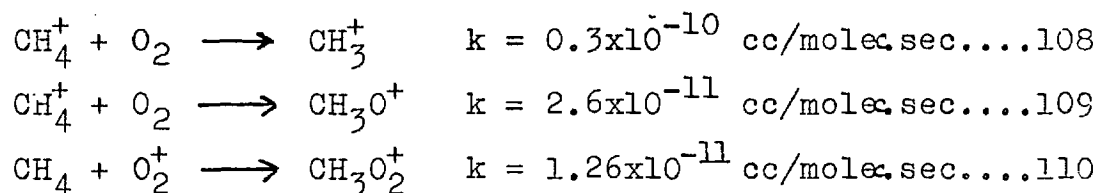


From results obtained from the radiolysis of methane plus deuterated hydrocarbon additives and oxygen, reactions of secondary product ions with oxygen were suggested (24). Reductions in the yield of ethane occurred when nitric oxide or oxygen were used as scavengers, and reactions between ions and the scavengers were postulated. The products of these reactions were not ascertained, but reaction 66 was put forward as a possibility.



Munson et al. (27) found no positive evidence for reactions of CH_5^+ or C_2H_5^+ with oxygen in a high pressure (2 mm Hg) mass spectrometer. They state however, that very slow reactions might occur. Oxygen was found to react with the following ions; CH_4^+ , CH_3^+ , CH_2^+ , CH^+ and C^+ , these ionic reactions being observed in a mass spectrometer at pressures up to 2 mm Hg. No evidence was obtained for extensive charge transfer between CH_4^+ and oxygen.

In a later paper (26) the ions CH_5^+ , C_2H_5^+ , C_2H_4^+ , C_3H_5^+ , and C_3H_7^+ were stated not to react rapidly with oxygen, and the low reactivity of CH_5^+ was conclusively demonstrated. The ions CH_3O^+ and CH_3O_2^+ were observed as second order product ions in methane plus 1% oxygen in the mass spectrometer at 2 mm Hg. CH_4^+ plus oxygen gives rise to CH_3^+ and CH_3O^+ . Methane plus O_2^+ yields CH_3O_2^+ , which is possibly protonated formic acid (26).



From considerations of the known rates of reaction for various ions with oxygen, Munson concluded that the concentration of oxygen would have to be quite high for there to be any noticeable effect on the product yields. Firstly, it should be noted that the residence time in the

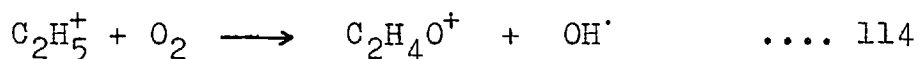
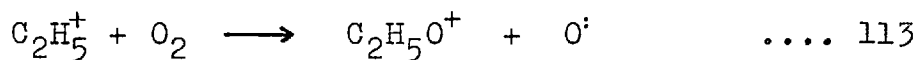
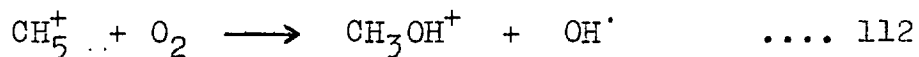
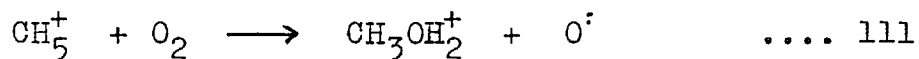
collision chamber of a mass spectrometer at 2 mm Hg is of the order of 10^{-5} second (79). Reactions between ions and oxygen may well occur too slowly to be noticed inside the collision chamber. However in an irradiated static system, reactions that are too slow to be observed in a mass spectrometer could conceivably be important. Secondly, in the normal radiolytic oxidation of methane the concentration of oxygen is about 2%. When small quantities of the higher hydrocarbon products have been formed, the ratio of oxygen to hydrocarbon ion scavenger is very large (of the order of 10^5 or more). This state fulfils Munson's conditions, namely that $[O_2]/[RH]$ should be greater than about 20, and hence reactions between ions and oxygen are to be expected.

Munson also suggested that part of the observed decrease in the hydrocarbon product yields brought about by oxygen (26), may be due to very rapid proton transfer to the water formed in the radiolysis. Proton transfer to the water molecules very efficiently removes the major ions CH_5^+ and $C_2H_5^+$ (Fig.5 page 36). The proton affinities of most of the simple oxygenated hydrocarbon derivatives are greater than that of water, and these probable products should therefore be very effective ion scavengers.

Both water vapour and the oxygenated products are, however, present in very small concentrations at low

conversions normally used in the radiolyses. They cannot therefore seriously be expected to exert a significant effect on the ion distribution, unless the rate constants for reaction with oxygen are much lower than the upper limits assigned by Munson et al.

Some reactions which are thermochemically feasible, but which have not been observed in mass spectrometer studies are:



CHAPTER II

EXPERIMENTAL TECHNIQUES.

Section.		Page
1.	Gamma Source, Irradiation Vessels, and Materials.	69
2.	Design and Operation of the Vacuum Line.	70
3.	Purification of Reactants, and Filling of the Irradiation Vessels.	71
3.1	Methane Purification.	71
3.2	Ethane, Ethylene, and Propane Purification.	72
3.3	Propylene Purification.	73
3.4	Oxygen Purification.	73
3.5	Nitrous Oxide Purification.	73
3.6	Filling procedure.	73
4.	Cleaning of the Irradiation Vessels.	74
5.	Irradiation and Photolysis Procedure.	74
6.	Dosimetry.	75
7.	Analysis of Irradiation Products Using Gas Chromatography.	76
7.1	Analysis of non-Oxygenated products.	76
7.1.1	Hydrogen, Oxygen and Nitrogen.	76
7.1.2	Saturated and Unsaturated Hydrocarbons C_1 to C_4 .	78
7.2	Analysis of Oxygenated Products; Methanol and Ethanol, Acetaldehyde and Formaldehyde.	79

Section.		Page
8.	Calibration of Gas Chromatography Apparatus.	80
8.1	Hydrocarbon and Other Gases.	80
8.2	Oxygenated Products; Methanol and Ethanol, Acetaldehyde and Formaldehyde.	82
9.	Colorimetric Analysis for Hydrogen Peroxide, Methyl Hydroperoxide, and Formaldehyde.	83
10.	Determination of Polymer Yield.	86
11.	Procedure for Radiolyses carried out at -78°C .	87
11.1	Oxygenated Products.	87
11.2	Hydrogen and Hydrocarbon Products.	88

Section 1. Gamma Source, Irradiation Vessels, and Materials.

Initially an 850 curie cobalt 60 gamma-ray source was used to irradiate the samples. Towards the end of the work a 17340 curie source became available and was used for the radiolyses.

Irradiations were carried out, at 765 mm Hg pressure at room temperature, and at -78°C , in cylindrical vessels of 70 ml to 100 ml, and of 600 ml capacity. The latter were used to obtain the yields of the oxygenated carbon products, and also initially the hydrocarbon products. When a second position became available in the 850 cobalt 60 source room, due to restricted space smaller vessels were used to determine the yields of the hydrocarbon products, hydrogen, and the decrease in oxygen concentration. This enabled work to proceed at a much faster rate than if the larger vessels only had been used.

For the mercury photosensitised oxidations at 100°C to 120°C , and polymer determinations, silica vessels were used.

The methane used throughout, obtained from L'Air Liquide of Belgium, was 99.95% pure. The oxygen concentration was given as 30 p.p.m, and the humidity, less than 5 mg/m^3 . Other gases were obtained from the British Oxygen Company.

Chemicals and laboratory reagents used in the analyses were of 'Analar' grade. The water used to

dissolve the oxygenated products from the radiolyses, and to make up reagents, was distilled from alkaline permanganate and then redistilled.

Section 2. Design and Operation of the Vacuum Line.

The vacuum line was designed to evacuate the irradiation vessels prior to filling with reactants, to trap out and purify the reactants, and to analyse the gaseous products from the radiolyses.

The pumping system consisted of a single stage oil diffusion pump, backed by an Edwards 1 SP 30 B rotary vacuum pump. An oil diffusion pump was used to avoid contaminating the system with mercury vapour. For the same reason the pressure gauges were of the Bourdon Tube type, or Pirani type, the former for pressures over the range 1 to 1000 mm Hg, and the latter for pressures from 10^{-5} to 1 mm Hg.

During the course of the work several modifications were made to the original design, the final design being shown in Fig.7. Gases to be purified were condensed into trap A, and distilled from trap to trap until the desired purity was obtained. The reactants were stored either in the 5 litre bulb, or as liquids in traps A B or C, using liquid nitrogen as the coolant.

The gas analysis section of the vacuum line consisted of traps to condense out the hydrocarbon products of the radiolyses, a Toepler pump, and a gas burette. A gas

sample vessel was attached to the top of the gas burette, via a standard B 10 Quickfit joint. The gas burette was only used to determine the P-V-T of carbon dioxide obtained from oxidising the polymer; all other products were measured quantitatively using a Perkin-Elmer Gas Phase Fractometer Model 452.

Section 3. Purification of Reactants and Filling of Irradiation Vessels.

The purification section of the vacuum line was evacuated to a pressure of the order of 10^{-4} to 10^{-5} mm Hg, and the section was then isolated from the rest of the system. The line between the point F and the pump (Fig.7 page 90) was flushed out with the gas to be purified, and then evacuated to 10^{-4} mm Hg. The gas was then condensed into trap E which was cooled in liquid nitrogen, until the required amount of gas had liquified or solidified.

Section 3.1. Methane Purification.

Methane was condensed into trap E, using liquid nitrogen to cool the trap, until about 25 ml had liquified. The trap was then allowed to warm up until approximately one third of the methane had distilled off. This first fraction was discarded. The next third was distilled into trap C and liquified, and the residual fraction in trap E was discarded. The purity of the gas thus obtained was of

the order of 99.999%. In order to measure accurately the yields of the hydrocarbons obtained at very low conversions, the concentration of the impurities had to be reduced still further. Continued trap to trap distillations, using liquid nitrogen-methanol mushes at about -100°C , improved the purity. The main impurity was ethane at about $10^{-5}\%$.

Section 3.2. Ethane, Ethylene and Propane Purification.

Far more care had to be taken in the purification of these gases, since the concentration of the impurities was much higher than that in methane (Appendix I page 172).

The required volume of gas was condensed into trap E, wherein it solidified. The pressure above the solid was reduced to about 10^{-2} mm Hg to remove any non-condensable gases. The trap was then allowed to warm up, and the first third of the gas which distilled over was discarded. The trap was then cooled using a liquid nitrogen-methanol mush, at about -100°C in the case of ethane and ethylene, or -80°C in the case of propane. The middle fraction was distilled over into trap A or B (cooled in liquid nitrogen), and the remaining third discarded. The trap to trap distillations were carried out on the collected fraction, until the impurity level was reduced to less than $10^{-3}\%$.

Section 3.3. Propylene Purification.

The propylene obtained from British Oxygen contained appreciable quantities of propane and the butanes. The purification was carried out as for propane above. The gas was collected in trap C and removing the liquid nitrogen coolant, the middle fraction was refluxed in trap C using the central tube in the trap to recondense the gas. The refluxing lasted for a few minutes, and each time the first fraction of the gas leaving the trap was pumped off and discarded.

Section 3.4. Oxygen Purification.

Medical oxygen was used throughout this work and was purified as for methane above. The main impurity was water vapour. No hydrocarbons, nor any of the permanent gases were detected in the purified oxygen.

Section 3.5. Nitrous Oxide Purification.

This gas was trapped out in trap E, using liquid nitrogen to cool the trap, and several freeze-pump-thaw cycles were sufficient to remove the non-condensable gases.

Section 3.6. Filling Procedure.

The irradiation vessels were attached to the vacuum line at the filling points F (Fig.7 page 90) via Quickfit joints, and evacuated to pressures of between 10^{-4} and 10^{-5} mm Hg. Traps A or C were opened to the main vacuum

line, the liquid in the trap allowed to evaporate into the line, and the vessels were filled to the required pressure. Prior to and during the filling, trap E was cooled in liquid nitrogen or a mush to exclude mercury vapour from the vessels.

Mixtures of the reactants were made up on a pressure basis using the Appleby and Ireland gauge, or the Pirani gauge to measure the pressure.

Section 4. Cleaning of the Irradiation Vessels.

The high vacuum grease (Apiezon L from Edwards Ltd.) was removed from the taps on the vessels, using carbon tetrachloride. The vessels were rinsed out twice with carbon tetrachloride, and the remaining solvent steamed out by boiling a few ml of distilled water in the vessels. Any residual organic matter was removed using hot chromic acid, the vessels were rinsed several times with distilled water, heated at 350 to 450°C, and then purged with oxygen whilst still hot. The vessels were then evacuated to 10^{-4} to 10^{-5} mm Hg and held at this pressure for at least 30 minutes, with liquid nitrogen coolant at traps E and M.

The silica vessels were annealed at 580°C after cleaning, and then evacuated.

Section 5. Irradiation and Photolysis Procedure.

Cobalt 60 was used as the source of gamma radiation. Initially an 850 curie source was used, the vessels being placed in fixed positions as near to the source sheath as

possible. Towards the end of the work a cobalt 60 source of 17340 curie strength became available. An aluminium holder was made to hold the vessels in fixed positions with respect to the source tubes, which fitted into recesses in the aluminium holder.

For the photolyses a Hanovia medium pressure mercury lamp was used. The silica vessel was placed on a thermo-controlled heating plate about 2cm from the lamp and the temperature was measured in a similar pyrex vessel equidistant from the lamp. The thermometer being fixed in the pyrex vessel via a B 14 Quickfit joint.

Irradiations were carried out at -78°C by surrounding the vessels with cardice-methanol mushes.

Section 6. Dosimetry.

The energy absorbed by the reactants exposed to the gamma radiation was determined using the Fricke Dosimeter. The dose-rate in the gas was calculated from that obtained using the Fricke Dosimeter, correcting for electron density difference between water and methane.

The yield of ethane obtained on irradiating methane at 760 mm Hg, and the yield of nitrogen from nitrous oxide irradiated at 760 mm Hg and 20°C , were also used as check on the results obtained from the Fricke Dosimeter.

The G-values used in the calculation of the dose-rates were: for the methane dosimeter, $G(\text{C}_2\text{H}_6) = 2.1$ (8, 18, 29, 33, 35), and for the nitrous oxide dosimeter $G(\text{N}_2) = 11.9$ (68, 69, 70, 71).

Section 7. Analysis of the Irradiation Products by Gas Chromatography.

All of the products, except for formaldehyde, methyl hydroperoxide, hydrogen peroxide, and carbon dioxide from burning the polymer, were measured quantitatively using a fractometer. The hydrocarbons, methanol and ethanol, and the aldehydes, were detected using the flame ionisation detector. The permanent gases were detected using the thermistor detector. The fractometer and the associated calibration sections are shown in Fig. 6 page 89.

Colorimetric methods were used to determine the yields of methyl hydroperoxide, hydrogen peroxide, and formaldehyde. The yield of carbon dioxide was measured using P-V-T measurements from the gas burette.

Section 7.1. Analysis of the Non-oxygenated Products.

Section 7.1.1. Hydrogen, oxygen, and nitrogen.

The irradiated vessel was attached to the analysis section of the vacuum line at point G (Fig.7 page 90), and the line evacuated to a pressure of about 10^{-5} mm Hg. Using liquid nitrogen as the coolant, the condensable products were condensed into trap J. With trap H cooled in liquid nitrogen, the coolant was removed from trap J, and the condensed gases evaporated under reduced pressure to form a thin uniform film of solid on the walls of trap H. With trap J cooled in liquid nitrogen, the non-condensable gas remaining in the radiation vessel and in

the line, was transferred to the gas burette using the Toepler pump. A mercury diffusion pump was initially used to transfer the gas, but was soon discarded due to mercury spreading into the main section of the vacuum line past trap J.

Occluded gas trapped in the condensed reactants and products in trap H, was removed by the freeze-pump-thaw cycle. Four cycles were found to be sufficient to remove all of the trapped gas.

The pressure of the gas collected in the gas burette was measured at known volumes, and the gas then transferred to the larger loop of the sample vessel (Fig.10 page 91). The sample vessel was attached to the gas sampling valve on the Perkin-Elmer Fractometer Model 452, using brass B 10 cones having $\frac{1}{8}$ " O.D. stainless steel tubing soldered into the ends (Fig.10 page 91), a copper template fitted over the tubes, and the sample vessel was held firmly onto the brass cones using rubber bands. The smaller loop of the vessel was evacuated, using the 1 SP 30 B single stage rotary vacuum pump attached to the calibration section (Fig.6 page 89), and the carrier gas then passed through that loop. The mode of operation of the gas sampling valve is shown in Fig.11 page 92..

After the carrier gas had been passed through the smaller loop for a few minutes to flush out any residual gas in the loop, the taps on the sample vessel were

turned through 180° and the products flushed into the chromatography column. To maintain similar conditions to those used in the calibration, the gas sampling valve was turned back to its original position 10 to 20 seconds after the products had been flushed into the column. This was found to be necessary because grease from the taps on the sample vessel collected in the entrance to the loops and thereby restricted the flow of the carrier gas.

Analyses for hydrogen, oxygen and nitrogen were carried out on molecular sieve columns 2m and 6m long, at 35°C and 30 to 45 ml/min carrier gas flowrate. For the hydrogen analyses, argon was used as the carrier gas. For the oxygen and nitrogen analyses, hydrogen was used as the carrier gas. In both cases, the thermistor detector was used to detect the gases.

Section 7.1.2. Saturated and Unsaturated Hydrocarbons
 C_1 to C_4 .

The products which were condensed into trap H (see above) were analysed as for the non-condensable products above after the bulk of the reactants had been removed by pumping. The pressure above the condensed products was reduced to about 0.3 to 0.35 mm Hg. The liquid nitrogen coolant was removed, and the gases transferred to the sample vessel as previously outlined, and then injected into the fractometer.

Analysis of the hydrocarbons was done on a 2m column of silica-gel plus 2½% di-2-ethyl hexyl sebacate, at 35 to 80°C and 25 to 55 ml/min carrier gas flowrate, depending upon the degree of separation required. The carrier gas used was argon, in conjunction with the flame ionisation detector.

Section 7.2. Analysis of Oxygenated Products;
Methanol and Ethanol, Acetaldehyde and
Formaldehyde.

These compounds were analysed separately from the other products, the radiolyses had to be repeated specifically to measure these products and also to measure hydrogen peroxide and methyl hydroperoxide.

The irradiated vessel was attached to the vacuum line via the sample vessel, at G, Fig.7 page 90 and the line evacuated to about 10^{-5} mm Hg. The products were then condensed into the larger loop of the sample vessel using liquid nitrogen as the coolant. With trap E cooled in liquid nitrogen, the pressure above the products was then reduced by pumping to about 0.5 to 1 mm Hg, the sample vessel isolated, and attached to the gas sampling valve on the fractometer. When the sample vessel had warmed up to room temperature, the products were flushed into the column.

The columns used to separate the compounds were, polyethylene glycol on chromosorb P (D E 105), and tetraethylene glycol dimethyl ether on teflon (D E 125). The

latter was found to be unsuitable due to bleeding, and was only used on two occasions. Column D E 105 was operated at 20 to 40 ml/min argon flowrate, and over the temperature range 35 to 80°C. The major hydrocarbons showed very little affinity for the column substrate, and all appeared within 7 seconds of the ethane peak.

The peaks for formaldehyde and methyl hydroperoxide coincided, and correction for the presence of a small amount of formaldehyde was made.

Methyl hydroperoxide could not be detected using the flame ionisation detector.

Retention times for all of the products analysed under different conditions of temperature, flowrate of carrier gas, and columns are given in Appendix II pp. 173, 174, and 175.

Section 8. Calibration of Gas Chromatography Apparatus.

Section 8.1. Hydrocarbons and other gases.

The fractometer and the calibration section were separate from the main vacuum line. The latter comprised two filling points, two storage bulbs, the gas sampling valve, and a rotary vacuum pump. Fig.6 page 89.

The amount of gas which would give a full scale deflection on the recording apparatus was very small, of the order of 5 μ l of gas at N.T.P. The smallest volume of gas that could be injected into the fractometer was

0.25 ml, the sample gases had therefore to be diluted.

The system used to prepare the calibration mixtures was to fill the 5 litre mixing bulb B, with the sample gas at a pressure of about 50 to 80 mm Hg, and then increase the pressure to atmospheric by introducing the carrier gas into the bulb. This gave mixtures of 7 to 10% concentration, and by repeating this operation several times (i.e. reducing the pressure after mixing to about 70 mm Hg and then adding carrier gas to bring the pressure up to atmospheric) any desired concentration could be obtained. The pressures were measured using a cathetometer. To ensure good mixing in the bulb, the inlet and outlet tubes were perforated. The first storage vessel used had a large limb protruding downwards from the base, which was cooled in liquid nitrogen and then allowed to warm up to room temperature after each addition of carrier gas. Repeated freezing out and warming up of the diluted mixtures promoted reasonable mixing of the sample gases with the diluent. The mixing was not however 100% reliable in the case of the higher hydrocarbons, and the bulb was redesigned as above. The concentration of the sample gases in the mixtures was of the order of 0.01 to 0.08%. Mixtures were made up containing approximately the same proportion of the gases as was expected to be found in the irradiated gas.

Quantitative measurement of the product yields was

carried out initially on a peak height basis. The peak height taken was the distance between the apex of the peak and the base line. This method was found to be not entirely satisfactory because the shape of the peak was dependent upon the injection pressure, and the size of the sample injected. The area between the curve traced out and the base line was then used for all quantitative measurements. The areas of unresolved peaks were obtained by the method of approximating triangles, given in the Principles and Practice of Gas Chromatography (Ed. L.Pecsok) p.147-8. The initial calibration charts were drawn of the molecules of each component injected, at N.T.P. plotted against the peak height divided by, or multiplied by, the range setting. The later charts were based on molecules plotted against peak area. The accuracy of the analyses using areas as the basis of quantitative measurement was about 5 to 7%, provided the characteristics of the chromatography apparatus remained unaltered. Calibration was carried out before and after measurement of the product yields.

Section 8.2. Oxygenated Products, Methanol and Ethanol, Acetaldehyde and Formaldehyde.

These compounds were measured on an area basis. Having relatively long retention times, a given amount could on occasions give rise to low and diffuse peaks, even though the conditions of analysis were kept constant.

Calibration was carried out by injecting standard

solutions of each compound separately. The solutions of the alcohols and aldehydes were made up volumetrically. The concentration of the aldehydes was measured colorimetrically (see below). Injections were of 1 to 10 microlitre of the standard solutions, using a Hamilton syringe. Larger volume injections saturated the thermistor and flame ionisation detectors with water, which then required about 30 minutes to restabilise.

Section 9. Colorimetric Analysis for Hydrogen Peroxide, Methyl hydroperoxide, and Formaldehyde.

Initially the hydrocarbon products were removed from the products condensed in a trap attached to the vacuum line, and water was added to the trap (Fig.8 page 91) whilst it was still cooled in liquid nitrogen. The trap was then allowed to warm up to room temperature. The oxygenated products were dissolved in 12 to 25 ml of water, depending upon the concentration of the products. The water was added in three aliquots to ensure that all of the compounds were dissolved, and that none remained in the trap. This method gave rise to rather erratic results, and it was decided to carry out a series of radiations specifically to determine the yields of the above compounds. The products were condensed out in the irradiation vessel using liquid nitrogen, most of the reactants pumped off, and the water added directly to the products condensed on the walls of the vessel.

The rate of oxidation of iodide by peroxides in the presence of an excess of the iodide, was used to characterise the peroxide products (~~70~~). This method gave the total peroxide concentration, including hydrogen peroxide if present.

Equal volumes of solutions A and B (see below) were mixed prior to analysis, and 5 ml of this mixture was added to an equal volume of the peroxide solution. Optical density changes at 350 m μ , measured against a reagent blank of 5 ml of water plus 5 ml reagent, were then followed and a first order plot made. The concentration of the peroxide was determined from the optical density measured after allowing the blank and the test solution to stand for at least 15 hours. Beer's law was not obeyed above optical densities of 0.8 (46), and measurements were therefore made below this limit, using an extinction coefficient of 11400.

Solution A. 33g of Potassium Iodide
 lg of Potassium Hydroxide
 0.lg of Ammonium Molybdate in 500ml of water.

Solution B. 10g of Potassium Hydrogen in 500ml of
Phthalate. water.

Pure methyl hydroperoxide was prepared by reacting dimethyl sulphate with alkaline hydrogen peroxide solution (73). The excess hydrogen peroxide was removed by distillation from a titanium sulphate reagent (see below) under vacuum. The distillate did not contain any formaldehyde as

indicated by the D.N.P.H. reagent. The resulting solution was made alkaline with sodium hydroxide solution, and dissolved in a small quantity of water, which was then acidified, and the methyl hydroperoxide was distilled off under vacuum and collected. First order plots led to a rate constant of $k = 0.022 \pm 0.002 \text{ min}^{-1}$ for the pure hydro peroxide.

Formaldehyde was determined using the method of Johnson and Scholes (74). 2ml of a 0.25% 2:4-dinitro-phenyl hydrazine (D.N.P.H.) solution in 30% perchloric acid were added to 10ml of the product solution and left to stand for 30 to 40 minutes. The hydrazone compound formed, was extracted with 10ml of carbon tetrachloride and separated from the aqueous layer. To this solution 10ml of absolute alcohol were added, and then 1 ml of a 0.1 N sodium hydroxide in ethanol solution, and the mixture shaken vigorously. The optical density was measured against water at 430 mμ exactly 2 minutes after commencing shaking. A blank observation was also carried out using 10 ml of water and 2 ml of the D.N.P.H. reagent and extracted as above, similarly measured against water. The difference between the two optical densities was divided by 10^{-7} to give the concentration of the aldehyde in moles per ml.

Formaldehyde was also estimated using the chromotropic acid method of Satterfield et alia (75). Methyl hydroperoxide was found to interfere with this method, decomposing

to form formaldehyde and indicating a higher yield of the aldehyde than was initially present.

The total peroxide yield was measured using the iodide method. The concentration of hydrogen peroxide was also determined colorimetrically. The methods employed were the development of the yellow colour on the addition of a titanium sulphate reagent (76), and measuring the peroxide concentration after having destroyed the hydrogen peroxide by the addition of catalase.

The titanium sulphate reagent was prepared by digesting 1 g. of anhydrous titanium dioxide with 100 ml of analar sulphuric acid for 15 to 16 hours at 150°C. The solution was then cooled, diluted one part solution to four parts water, and filtered. A few drops of dilute hydrogen peroxide were added to the solution before use. 2 ml of this reagent were added to 23 ml of the product solution, and the optical density measured at 405 $m\mu$ using 4 cm. glass cells. The calibration factor used, was an optical density of 2.45 is equivalent to 10^{-3} moles/litre.

Section 10. Determination of Polymer Yield.

The radiolyses were carried out in a silica vessel of volume 97 ml, having a water condenser as an integral part of the vessel Fig.9 page 91.

The vessel was attached to the vacuum line at point K (Fig.7 page 90). The products were condensed out in the

vessel using liquid nitrogen, and the pressure reduced to as low a value as possible. The coolant was changed successively to cardice-methanol and ice, and the pressure reduced after each change of coolant to about 10^{-6} mm Hg. Purified medical oxygen was expanded from trap E into the vessel to a pressure of 150 mm Hg, and the polymer adhering to the walls of the vessel was burnt off at 600 to 800°C. When the vessel had cooled sufficiently, it was cooled in liquid nitrogen to condense out the carbon dioxide, and the unconsumed oxygen was pumped off. The carbon dioxide was transferred to trap J, and with a cardice-methanol mush replacing the liquid nitrogen at trap J, the gas was pumped across to the gas burette where the P-V-T was measured.

The water condenser was necessary to ensure that none of the grease on the B 10 cone connection was burnt off, thereby increasing the carbon dioxide concentration.

Section 11. Procedure for Radiolyses carried out at -78°C.

Section 11.1 Oxygenated products.

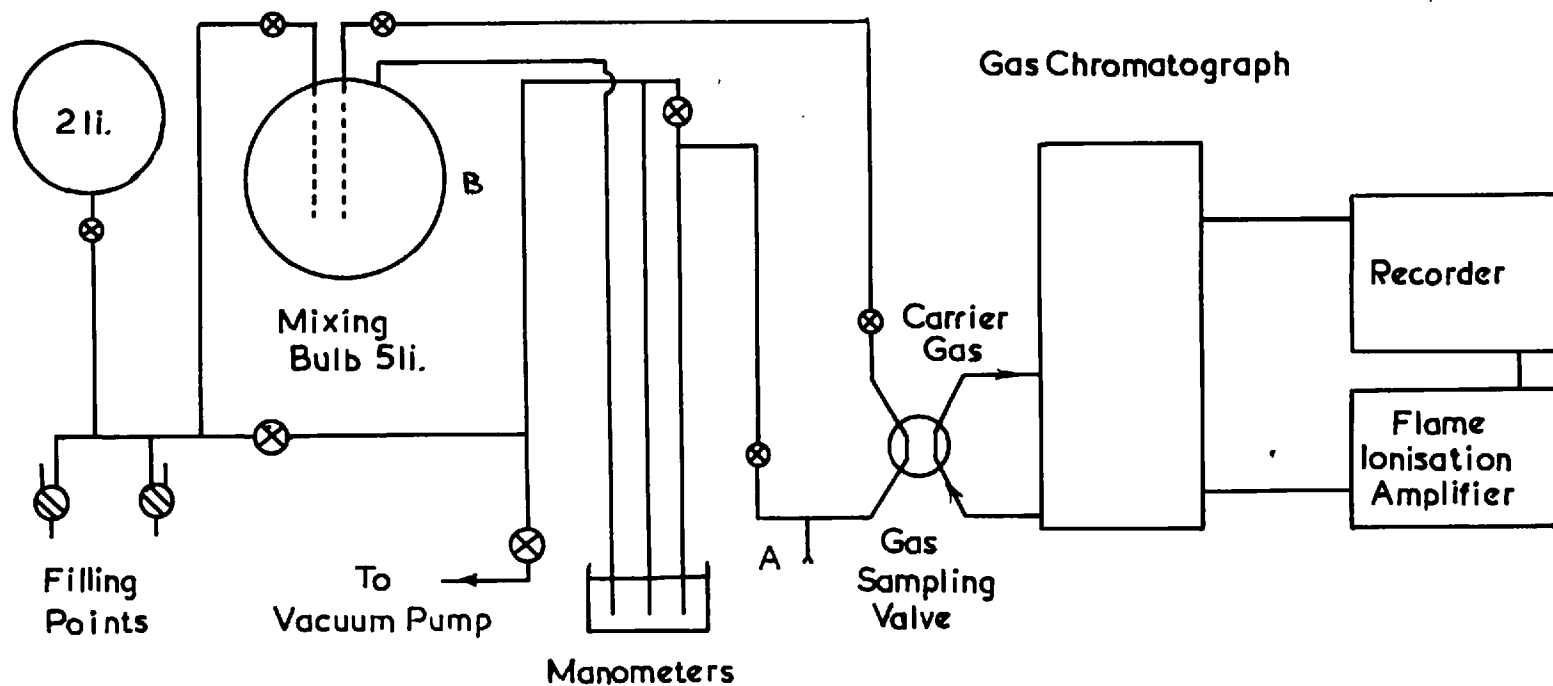
The vessels to be irradiated were placed in a large vacuum flask in a fixed position near to the 850 curie cobalt 60 source. The vacuum flask was then filled with a cardice-methanol mush, and topped up as the cardice evaporated. It was also necessary to compact the cardice occasionally. The vacuum flask was insulated by wrapping

asbestos rope around the outside, and an asbestos cover was used to minimise evaporation from the surface.

The irradiation vessel was not allowed to warm up after irradiation. The vessel was attached to the vacuum line, the products condensed out in the vessel, and the pressure above the products reduced to about 1 mm Hg. 12 to 25 ml of water were added in aliquots of about 4 ml to dissolve the products.

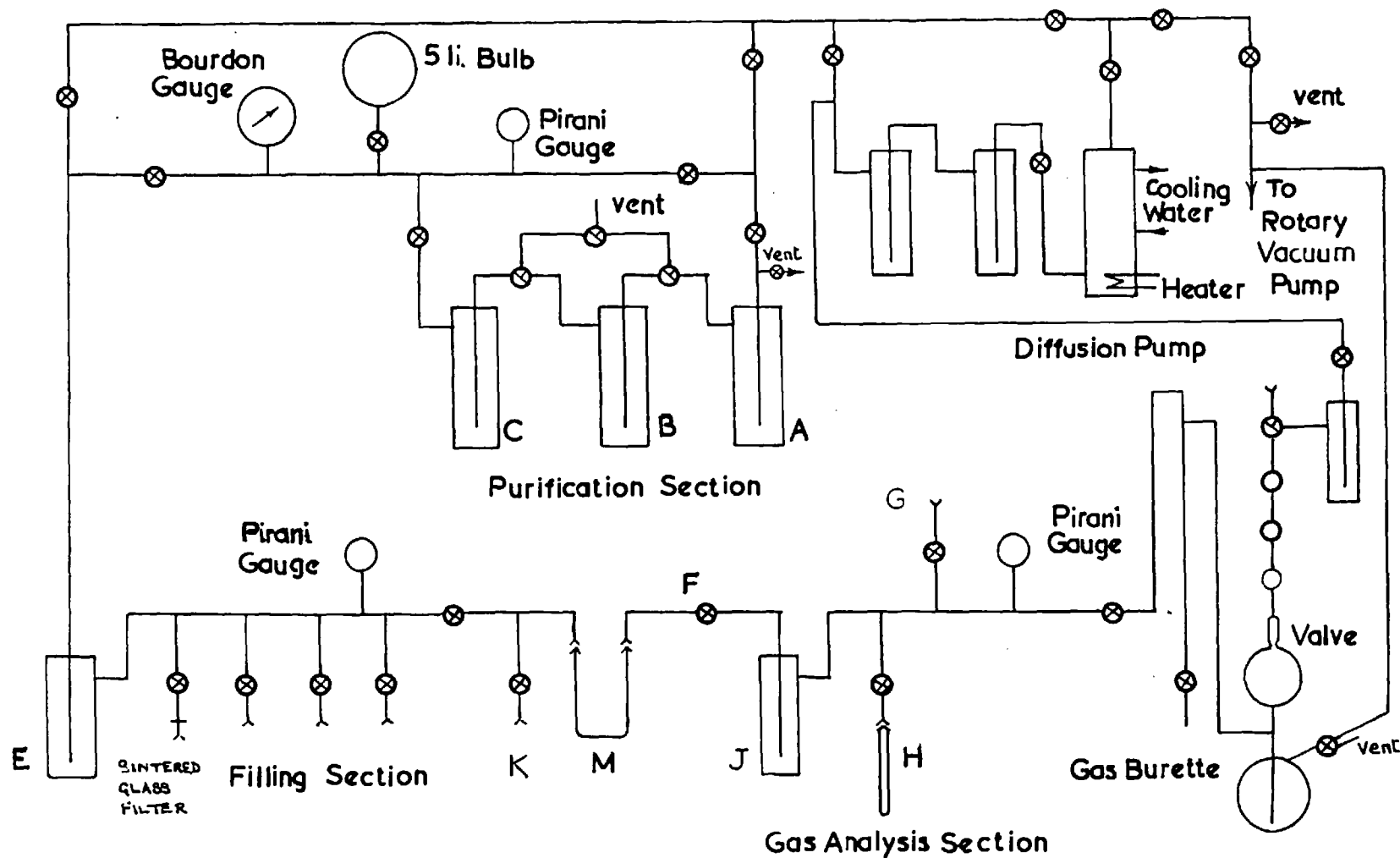
Section 11.2 Hydrogen and hydrocarbon products.

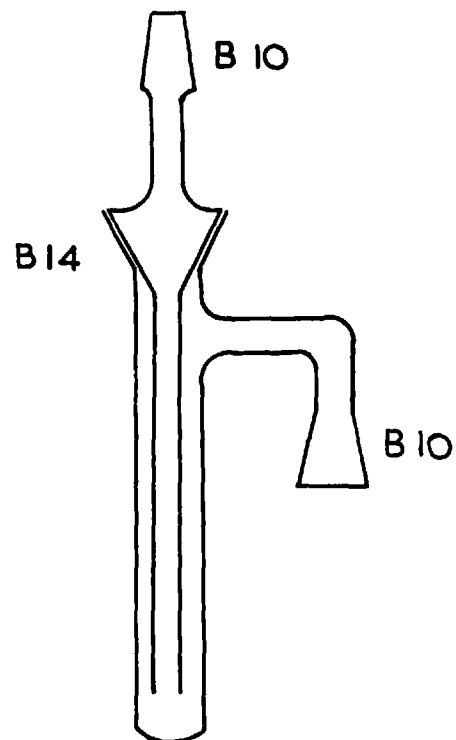
The smaller vessels were used to determine the yields of these compounds, using the larger cobalt 60 source. An aluminium holder was built specially for these irradiations. The radiolyses were of one to four hours duration. Instead of placing the unit in a vacuum flask, the holder was well insulated using asbestos rope, and was topped up with cardice (and the cardice compacted) every hour. The products were then analysed as described previously.



Calibration and Analysis Line
Fig. 6.

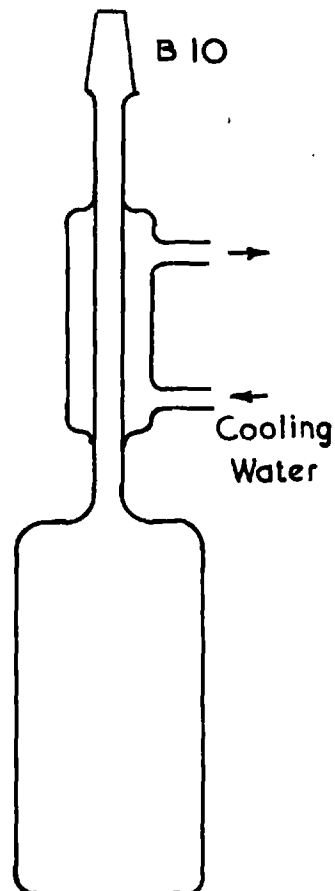
Fig. 7.





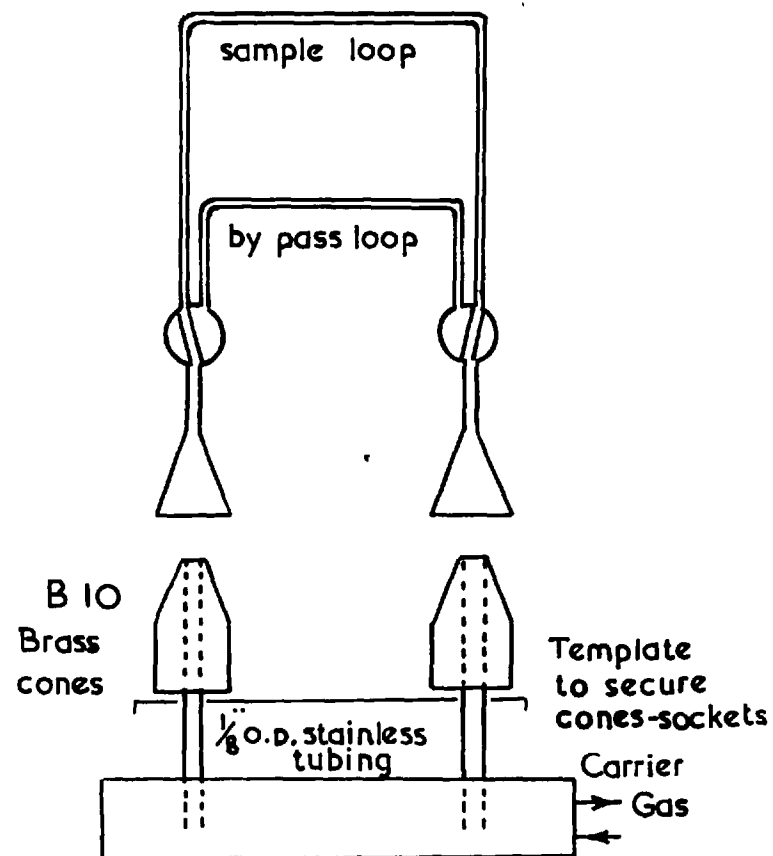
Trap used initially for
product collection

Fig. 8



Silica vessel used
for polymer determination

Fig. 9.



Sample vessel and
connections to sampling valve

Fig. 10

Selector knob

92.

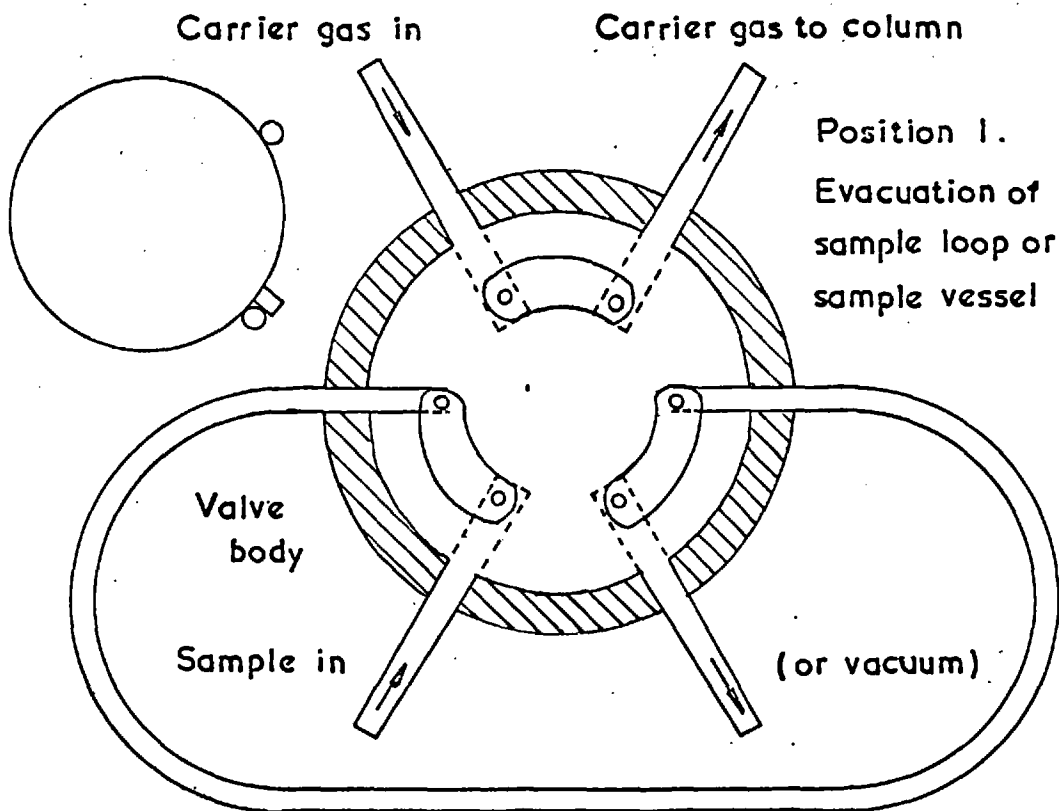
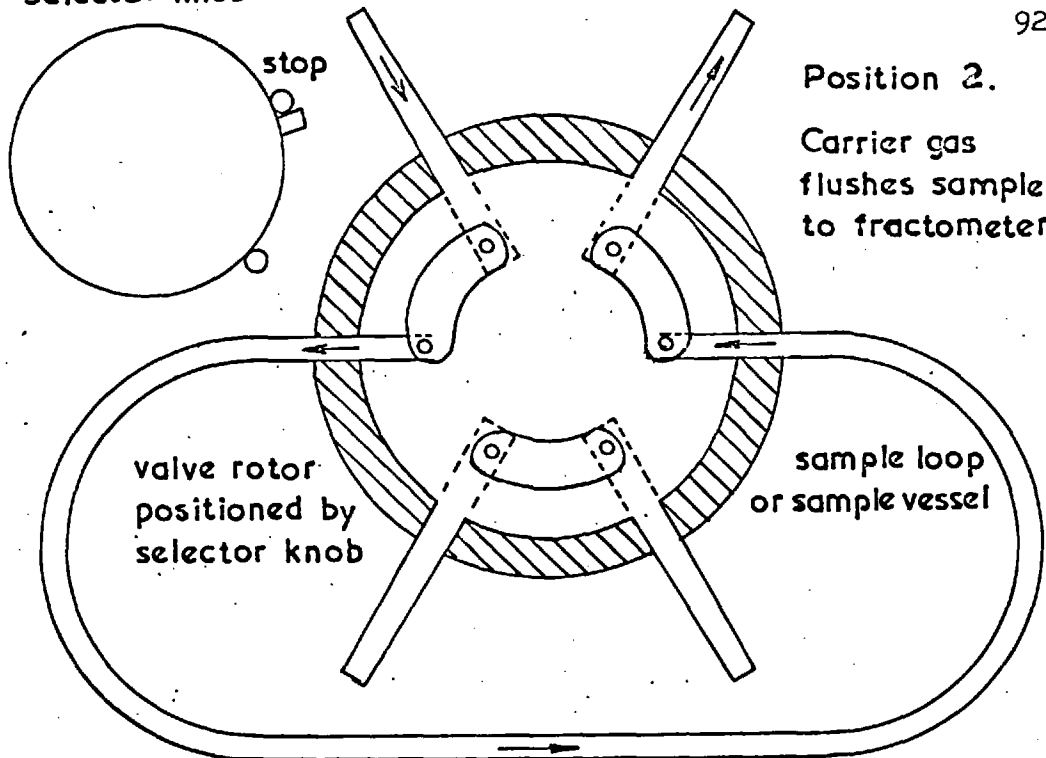


Fig.II
Gas Sampling Valve

CHAPTER III.

EXPERIMENTAL RESULTS.

Section.		Page
1.	Purity of Methane.	94
2.	Dosimetry.	94
3.	Dose-rates.	95
4.	Preliminary Irradiation of Methane at 20°C.	96
5.	Product Collection Efficiency.	97
6.	Polymer Yield.	98
7.	Irradiation of Methane at -78°C.	98
8.	Methane plus Additives.	99
8.1	Methane plus 0.6% to 2% Ethylene.	99
8.2	Methane plus 0.01% and 1% Propylene.	101
8.3	Methane plus 0.01% and 1% Propane.	101
8.4	Methane plus 0.3% and 1% Water Vapour.	102
8.5	Methane plus 1% Water Vapour and 2% Propylene.	103
8.6	Methane plus 0.026% and 2% Oxygen at 20°C, and Methane plus 2% Oxygen at -78°C.	103
8.7	Methane plus 2% Oxygen and 1% Water Vapour.	109
8.8	Methane plus 0.13% Ethylene and 0.39% Oxygen.	110
8.9	Methane plus Oxygen and Propane.	110
8.9.1	Hydrocarbon Products.	110
8.9.2	Oxygenated Products.	111
8.10	Methane plus 0.065% Oxygen, Oxygen Consumption.	113
8.11	Methane plus Mercury Vapour.	113
8.12	Methane plus 2% Oxygen and Mercury Vapour.	114
8.13	The Mercury Sensitised Photolysis of Methane, and Methane plus 2% Oxygen.	114

Section 1. Methane Purity.

The purity of the methane obtained by fractional distillation was greater than 99.9999%. The main impurity was ethane at a concentration of about $1 \times 10^{-5}\%$. Propane and higher hydrocarbons could not be detected, their concentration was therefore less than $5 \times 10^{-6}\%$, the limit of detection for the flame ionisation detector.

Section 2. Dosimetry.

The use of methane as a dosimeter, based on the ethane yield, was investigated. The G-value for the formation of ethane from methane was found to be 2.02, 5% less than that obtained by other workers, 2.1 (8,18, 29, 33, 35). The energy deposited in the methane was measured using the Fricke dosimeter. It was far more convenient to use the Fricke dosimeter rather than methane, and the dose-rates were always determined using the former. The dose-rate measured was corrected for the electron density difference between water and air, and the ratio of the stopping powers methane to air was used to calculate the dose-rate in methane. The result was then corrected for the 5% discrepancy in the ethane yield. Results from the Fricke dosimeter were reproducible to within 3%, whereas the fractometer measurements were only accurate to $\pm 5\%$.

As a check on the results from the above dosimeters,

the yield of nitrogen from the irradiation of nitrous oxide was determined. The G-value for nitrogen formation has been determined under various conditions of irradiation (68, 69, 70, 71), and a value of 11.9 was used in the present work. Results obtained for the dose-rate measured using the nitrous oxide, Fricke and methane dosimeters are given in Table 7. The agreement between the results obtained was very good.

Table 7.

Comparison of the Dose-rates obtained using the Fricke, Nitrous Oxide, and Methane Dosimeters.

Dosimeter Used	Dose-rate obtained eV/ml of CH ₄ /min
Fricke	9.79×10^{14}
Nitrous Oxide	9.22 "
Methane	9.32 "

Section 3. Dose-rates.

Using the 850 curie cobalt 60 source, the larger vessels received dose-rates of 0.84, 0.99 and, 1.34×10^{14} eV/ml/min. The smaller vessels could be fixed nearer to the source, and received dose-rates of 2.5 and 4.5×10^{14} eV/ml/min. Higher dose-rates were obtained from the 17340 curie source, 7.7 and 9.32×10^{14} eV/ml/min in the central and periphery positions respectively.

Section 4. Preliminary Irradiation of Methane at 20°C.

The initial few irradiations with pure methane were carried out at room temperature and 765 mm Hg pressure, at high doses, conversions were of the order of 0.3 to 0.5%. The irradiated vessel was attached to point A (Fig. 6 page 89) on the gas sampling line of the fractometer, and 5 ml of the reactant and products were injected into the column, at pressures of between 100 and 300 mm Hg. The concentration of the products injected was very low, and the flame ionisation detector had to be used on maximum sensitivity. Concentration of the products, by condensing them into the sample vessels (Fig.10 page 91), and pumping off most of the methane, made it possible to analyse the products formed at conversions as low as $10^{-4}\%$.

The products observed were hydrogen, ethane, ethylene, propane, iso-butane and normal butane, and the pentanes. Ethylene was only found to be present at the lowest conversions, corresponding to doses less than 4×10^{18} eV. The amount of the C_5 products was very small, and no quantitative measurements were made of these yields. The yields of all of the products except ethylene, were found to be independent of the dose-rate, and the dose received, Fig.12 page 116. The G-value for the formation of ethylene decreased rapidly with increasing dose over the range of dose studied, approximately 10^{18}

to 10^{21} eV. The G-values for the products whose yields were measured, are given in Table 8 page 100.

When the irradiated vessel was left overnight and the products analysed the following day, the yields of the higher hydrocarbons C_3 and C_4 were found to be less than those obtained when analysis was carried out immediately after irradiating. This was thought to be due to adsorption of these hydrocarbons on the grease on the stopcock. Greaseless stopcocks having neoprene diaphragms were used instead of the greased taps. For the higher conversions, this made no difference to the yields obtained. Provided that the vessels irradiated to very low doses, were analysed within a few hours of removing them from the source, no decrease in the yields was observed (compared with the yields obtained from vessels having diaphragm taps), and a greased tap could be used.

Section 5. Product Collection Efficiency.

The unreacted methane was pumped off from above the condensed reactants and products at -196°C , down to a pressure of approximately 0.3 to 0.4 mm Hg. Only traces of the most volatile product at -196°C (i.e. ethylene) were noted when the pressure above the products was reduced from 2 mm to 0.4 mm Hg, and this gas collected and analysed. The total percentage of products collected at the highest conversions of 0.3 to 0.5% was always greater than 96.0%

and generally greater than 99.0%. The melting points and boiling points and vapour pressures for various compounds are given in Appendix III page 176.

Section 6. Polymer Yield.

When pure methane was irradiated and the products were not condensed in the irradiation vessel, the walls of the vessel were easily wetted with water, except in the cases of the highest dose used, greater than about 3×10^{18} eV/ml.

The yield of polymer was determined by condensing the products onto the walls of the silica irradiation vessel (Fig.9 page 91), pumping off the methane and products as described above (page 87), adding oxygen and burning the polymer adhering to the walls to carbon dioxide. Irreproducible results were obtained, but the G-value for polymer formation based on $G(-CH_4)$ forming the polymer was of the order of 1 to 9.

Section 7. Irradiation of Methane at -78°C .

The hydrocarbon products were measured from the 600 ml vessels in conjunction with the 850 curie source at a dose-rate of 0.99×10^{14} eV/ml/min. Hydrogen was measured at dose-rates of 7.7 and 9.32×10^{14} eV/ml/min, using the smaller vessels of 100 ml capacity, in the 17430 curie source facility.

The yields of hydrogen, ethane, propane and isobutane, were all less than those obtained from methane

irradiated at 20°C, and all were found to increase linearly with increasing dose, Fig.13 page 117. The ethylene yield increased rapidly to a maximum, and gradually decreased with increasing dose received.

Section 8. Methane plus Additives.

In general the concentration of the additive was always less than 2%. Mixtures were made up on a pressure basis, the percentage of the additive being the partial pressure of the additive p_a , divided by the total pressure P_T , multiplied by 100.

Section 8.1 Methane plus 0.6 to 2% Ethylene, at 20°C and 765 mm Hg.

In order to be able to evaluate the products obtained from the system in which ethylene and oxygen are present (and both compete for the hydrogen atoms), methane was first irradiated in the presence of small amounts of ethylene.

Compared with the product yields from pure methane, the G-values of hydrogen and ethane decreased from 5.63 and 2.02 respectively to 3 and 1.26 respectively, those of propane, iso-butane, and normal butane increased. The G-values were found to be independent of the ethylene concentration over the range studied. Table 8 page 100.

Table 8

Initial G-values for Hydrogen and the Hydrocarbon Products
from the Radiolysis of Methane, and Methane plus Hydrocarbon Additives.

System.	<u>G-values</u>							
	CH ₄	CH ₄ +1%	CH ₄ +2%	CH ₄ +0.01%	CH ₄ +1%	CH ₄ +0.01%	CH ₄ + 1%	CH ₄ +1% C ₃ H ₆
Product.		H ₂ O	C ₂ H ₄	C ₃ H ₈	C ₃ H ₈	C ₃ H ₆	C ₃ H ₆	+ 1% H ₂ O
H ₂	5.63±0.5	6.1±0.5	3.0±0.2	5.24±0.5	-	2.7±0.2	2.7±0.2	n.d.
C ₂ H ₄	0.12	0.0	-	0.02	0.06	0.5±0.05	1.34±0.1	0.8±0.08
C ₂ H ₆	2.02±0.2	1.53±0.12	1.26	2.04±0.2	4.6±0.5	1.65±0.2	0.9 ± 0.1	0.5±0.05
C ₃ H ₈	0.19	0.37±0.04	1.31±0.1	0.33	-	1.03±0.1	1.09±0.1	0.75±0.07
iC ₄ H ₁₀	0.04	0.08	0.12	0.11	0.12	0.85±0.1	0.83±0.1	0.8 ± 0.1
nC ₄ H ₁₀	0.06	0.15	1.12±0.1	0.14	0.13	0.07	n.d	n.d.

n.d = not determined.

Section 8.2 Methane plus 0.01 and 1% Propylene, at 20°C and 765 mm Hg.

The effect of a second hydrocarbon hydrogen atom scavenger on the product formation from the radiolysis of methane, was studied using propylene as an additive. It was also necessary to determine the product distribution in the presence of propylene, since this hydrocarbon was used to remove hydroxyl radicals formed during the radiolysis of methane plus water.

The yields of the hydrocarbon products were dependent on the propylene concentration. The 100 ml vessels were used at a dose-rate of 0.4×10^{14} eV/ml/min, from the 850 curie cobalt 60 source. The G-values obtained at the two additive concentrations used, are given in Table 8 page 100.

Section 8.3 Methane plus 0.01% and 1% Propane, at 20°C and 765 mm Hg.

So as to be able to interpret the yields of the products obtained from the radiolysis of methane plus oxygen and propane, where propane is present to scavenge the ions CH_5^+ and C_2H_5^+ , a 'blank' experiment was performed using methane plus propane.

The presence of the smaller concentration of propane had little effect on the product yields. Increasing the percentage of the additive to 1, gave rise to an increase in rate of formation of ethane, $G(\text{C}_2\text{H}_6)$ was 4.6 at 1% C_3H_8 .

The G-values for the formation of the other products remained essentially constant, no acetylene was noted. A small amount of ethylene was found to be present at the highest dose, the G-value for which increased from 0.02 to 0.06 when the propane concentration was changed from 0.01% to 1%. The G-values obtained are given in Table 8..

Vessels of 90 ml capacity were used in the irradiations, which were carried out at a dose-rate of 0.4×10^{14} eV/ml/min, at 20°C and 765 mm Hg pressure.

Section 8.4 Methane plus 0.3% and 1% Water Vapour 20°C and 765 mm Hg.

Munson (26) suggested that water would efficiently remove the ions CH_5^+ and C_2H_5^+ , formed in the radiolysis of methane, giving rise to CH_4 and C_2H_4 respectively. To investigate this postulate, methane has been irradiated in the presence of water vapour.

The ethane yield was the only one which altered appreciably due to the presence of the additive, no ethylene was noted amongst the products. $G(\text{C}_2\text{H}_6)$ decreased from a value of 2.02 in pure methane, to 1.49, and $G(\text{H}_2)$ increased from 5.63 to 6.1. The rates of formation of all of the other products were found to be independent of the concentration of the additive over the range studied. No dose dependence was noted.

Section 8.5 Methane plus 1% Water Vapour plus 2% Propylene, 20°C 765 mm Hg.

Propylene was added to the methane plus water system, in order to investigate the effect of the hydroxyl radicals formed as a result water being present. The propylene also scavenges the hydrogen atoms formed.

The presence of the water vapour caused a decrease in the yields of the hydrocarbon products measured, except for iso-butane, the yield of which remained constant. The G-value for hydrogen formation was essentially the same as that obtained from the radiolysis of methane plus 2% propylene. The G-values for product formation are given in Table 8 page 100.

No dose effects were noted over the dose range 4.5 to 20×10^{18} eV. Irradiations were performed at 20°C and at a pressure of 765 mm Hg, in the 90 ml vessels, at a dose-rate of 0.4×10^{14} eV/ml/min.

Section 8.6 Methane plus 0.026% and 2% Oxygen at 20°C, and Methane plus 2% Oxygen at -78°C.

The experiment in which methane plus 0.026% oxygen was irradiated, was carried out to investigate the effect of a very small amount of oxygen on the product yields, to study the change in the rate of product formation as the oxygen is used up, and to determine a G-value for oxygen consumption.

The oxygen concentration was found to be too low to

be measured accurately, and a separate experiment was carried out to determine G ($-O_2$), section 8.10 page 113.

The G-values obtained for the hydrocarbon products are given in Table 9 below.

Table 9.

G-values for the Hydrocarbon Products from Methane plus Oxygen Irradiated at 20°C and -78°C.

System and Conditions.	<u>G-values</u>				
	CH ₄ +0.026% O ₂ 20°C	CH ₄ +2% O ₂ 20°C	CH ₄ +2% O ₂ -78°C	CH ₄ 20°C	CH ₄ -78°C
Product					
H ₂	2.75	2.75	2.55	5.63	3.3
C ₂ H ₄	0.43	0.46	0.12	0.12	0.14
C ₂ H ₆	0.2	0.135	0.14	2.02	0.46
C ₃ H ₈	0.012	0.01	0.06	0.19	0.2
iC ₄ H ₁₀	n.d.	0.02	0.005	0.04	0.005
nC ₄ H ₁₀	n.d.	0.005	0.1	0.06	0.002

The hydrocarbon product yields from methane plus 0.026% oxygen increased fairly linearly with increasing dose (Fig.14 page 118), until the oxygen was nearly all consumed. The ethylene yield passed through a maximum at a dose of $\sim 6 \times 10^{19}$ eV, and then decreased rapidly to become a trace quantity at doses greater than 8×10^{19} eV. At the point at which the ethylene yield is a maximum,

the rate of formation of ethane, propane and hydrogen, begin to increase rapidly. The G-values for these three products tend towards those obtained from methane at the highest doses used, $\sim 10^{19}$ eV.

The hydrocarbon yields were measured using the larger vessels (600 ml), at dose-rates of 0.99 and 1.3×10^{14} eV/ml/min. Hydrogen was determined using the 90 ml capacity vessels, at dose-rates of 7.7 and 9.32×10^{14} eV/ml/min. No dose-rate or vessel size (surface area) effects were noted.

The oxygenated products analysed quantitatively were, formaldehyde, methyl hydroperoxide, methanol and ethanol. The 600 ml vessels were used at a dose-rate of 0.99×10^{14} eV/ml/min, the G-values obtained are given in Table 10 page 106.

The rate of formation of the aldehyde product decreased as the concentration of oxygen was increased from 0.026% to 2%, at room temperature. The peroxide yield increased under these conditions. The yields of both formaldehyde and methyl hydroperoxide from methane plus 0.026% oxygen increased from zero to a maximum, and then decreased rapidly as the oxygen was used up, (Fig.15 page 119). The maxima appeared at approximately the same dose as did the maximum for the ethylene yield, and the points at which the ethane, propane, and hydrogen yields started to increase. Dose-yield plots for methyl

hydroperoxide and formaldehyde from methane plus 2% oxygen have been drawn, Fig.16 page 120.

Table 10.

G-values for the Oxygenated Products from Methane plus Oxygen Irradiated at 20°C and -78°C.

System and Conditions	<u>G-values</u>			
	CH ₄ +2%O ₂ 20°C	CH ₄ +0.026% O ₂ 20°C	CH ₄ + 2%O ₂ -78°C	
Vessel	600 ml	600 ml	600 ml	312 ml
Product				
H.CHO)	0.07	0.38	0.52	0.52
CH ₃ CHO)				
CH ₃ OH	1.07	n.d	0.62	0.62
C ₂ H ₅ OH	0.05	n.d	0.005	0.005
CH ₃ OOH	3.0	2.05	0.91	2.1
H ₂ O ₂	0.0	0.0	3.04	3.15
Ratio of H ₂ O ₂	-	-	3.35	1.5
	CH ₃ OOH	n.d. = not determined		

At -78°C both the aldehyde and peroxide G-values increased. The aldehyde product was not analysed for acetaldehyde content. The peroxide product consisted mainly of hydrogen peroxide. The amount of hydrogen peroxide present in the larger 600 ml vessels was just

over twice the amount obtained when using the smaller 312 ml vessels. No hydrogen peroxide was found to be present ^{in the products} obtained from the radiolysis of methane plus 0.026% or 2% oxygen, at room temperature.

The yield of hydrogen peroxide was determined using the titanium sulphate reagent and, measuring the total peroxide yield before and after destroying the hydrogen peroxide with catalase. The two methods showed very good agreement.

Method	Dose eV x 10 ⁻¹⁹	Vessel ml	H ₂ O ₂ molecules x 10 ⁻¹⁷	CH ₃ OOH molecules x 10 ⁻¹⁷
Catalase	2.9	312	8.48	5.72
Titanium Sulphate	"	"	8.19	5.72

Identification of the peroxide products was done by plotting the increase in iodine liberated from the iodide reagent, in terms of optical density, against time. From the first order plots obtained (Figs.17, 18, pages 121 & 122), the pseudo first order rate constant was obtained. The rate constant for pure methyl hydroperoxide was $0.022 \pm 0.002 \text{ min}^{-1}$, that for the peroxide product varied from 0.018 min^{-1} for the product from the radiolysis of methane plus 2% oxygen, to 0.023 min^{-1} for the product from methane plus oxygen plus water vapour.

The first order plots were linear, indicating that dimethyl peroxide was absent (46), but they did not

always pass through the origin. Hearne and Hummel suggested that, where hydrogen peroxide was present, the plots will not go through the origin (46). It was also proposed that the dilution of methyl hydroperoxide solutions below $3.3 \times 10^{-5}M$, leads to the formation of hydrogen peroxide.

Pure methyl hydroperoxide was prepared and first order plots made for solutions of various concentrations of the peroxide, both higher, and less than $3.3 \times 10^{-5}M$. In some cases the plots passed through the origin, and in others they did not. These results are not consistent with the idea that hydrogen peroxide is formed from methyl hydroperoxide when its concentration is less than a certain fixed value. In the presence of catalase the plots, at all methyl hydroperoxide concentrations and in every case for the product solutions, were linear and passed through the origin.

The rate of reaction of hydrogen peroxide with the iodide reagent is about 4 times greater than the rate for methyl hydroperoxide with the reagent (77, 78). If hydrogen peroxide is formed on diluting a solution of methyl hydroperoxide, initially containing only the hydroperoxide, then on adding the iodide reagent (or catalase) the concentration of hydrogen peroxide will be reduced more rapidly than that of methyl hydroperoxide. This should cause more hydrogen peroxide to be formed due

to the displacement of the equilibrium between the organic peroxide and hydrogen peroxide, by removal of the latter.

Section 8.7 Methane plus 2% Oxygen and 1% Water Vapour,
20°C and 765 mm Hg.

In the radiolysis of methane plus water vapour, no ethylene was found present as a product. Ethylene is removed by hydrogen atom attack, and oxygen has been added to protect any ethylene formed during the radiolysis from further reaction.

The hydrogen, ethane, aldehyde, peroxide, and ethanol G-values were the same as those obtained from the radiolysis of methane plus 2% oxygen. The G-value for ethylene formation increased to 0.86, whilst that for methanol decreased to 0.23 (from values of 0.46 and 1.07 respectively from methane plus 2% oxygen) Fig.19 page 123. A first order plot was made for the peroxide product (Fig.18 page 122). Without catalase the plot did not pass through the origin, and indicated that a small amount of hydrogen peroxide was present. This was confirmed since the addition of catalase caused the plot to go through the origin. The rate constant was the same for both first order plots.

The irradiations were carried out in the 600 ml vessels to determine the yields of the oxygenated products, and in the 90 ml vessels to measure the other product yields. The dose-rates used were 0.99×10^{14} eV/ml/min for

the larger vessels, and 0.4×10^{14} eV/ml/min for the smaller vessels. The G-values obtained are given in Table 11 page 112.

Section 8.8 Methane plus 0.13% Ethylene and 0.39% Oxygen,
20°C and 765 mm Hg.

The effect of the removal of hydrogen atoms by adding ethylene to compete with oxygen for these atoms was investigated in this experiment.

The concentrations of the additives were reduced to keep the total percentage of the additives less than 1%. The hydrogen, ethane, and butane yields, were similar to those measured in the cases of methane plus 0.026% and 2% oxygen, see Table 9 page 104 and Table 11 page 112.

A very small amount of acetylene was noted as a product, $G(C_2H_2) = 0.007$. Propylene was found to be present with a G-value of 0.25, slightly greater than $G(C_2H_6)$, which was 0.2.

Comparing the yields of the products, with those obtained from methane plus 2% oxygen, the aldehyde, peroxide, and ethyl alcohol G-values increased, the methyl alcohol yield decreased slightly. Conditions for the irradiations were the same as for section 8.7 above.

Section 8.9 Methane plus Oxygen and Propane.

Section 8.9.1 Hydrocarbon Products.

In this experiment the combined effect of a radical and ion scavenger was studied. The ratio of oxygen to

propane was kept constant at a value of 1:1, and the percentage of the additives varied over the range 0.01 to 2.0%. The hydrogen and ethylene rates of formation were found to be independent of the concentration of the additives, $G(H_2) = 3.34$, and $G(C_2H_4) = 0.43$. The G-value for ethane increased from a value of about 1 at 0.01% additive concentration, to 3.0 at 2% oxygen plus propane. The yield increased linearly over this range, Fig.20 page 124. The G-values for the products measured are given in Table 11 page 112.

Section 8.9.2 Oxygenated Products.

The ratio of oxygen to propane was 1:5, and the total concentration of the additives was 2%. Compared with the product yields obtained from methane plus oxygen, the aldehyde and peroxide yields both increased. There was also a small increase in the G-value of methyl alcohol, the ethyl alcohol yield could not be determined, due to interference from other compounds. The G-values obtained are given in Table 11 page 112.

The radiolyses were carried out at room temperature, at a pressure of 765 mm Hg, and at a dose-rate of 0.55×10^{14} eV/ml/min.

Table 11.

G-values for Initial Product Formation from
the Radiolysis of Methane plus Various
Additives.

System	<u>G-values</u>			
	$\text{CH}_4 + 2\% \text{O}_2$ $+ 1\% \text{H}_2\text{O}$	$\text{CH}_4 + 0.13\% \text{O}_2$ $+ 0.39\% \text{C}_2\text{H}_4$	$\text{CH}_4 + \text{O}_2$ $+ \text{C}_3\text{H}_8$	$\text{CH}_4 + 2\%$ O_2
Product				
H_2	2.7 ± 0.2	2.85 ± 0.2	3.34	2.7
C_2H_2	0.0	0.007	0.0	0.0
C_2H_4	0.85 ± 0.05	-	0.43	0.44
C_2H_6	0.155 ± 0.01	0.19	0.94	0.15
C_3H_6	0.0	0.245^*	-	0.0
C_3H_8	0.0	0.0	0.0	0.012
$i\text{C}_4\text{H}_{10}$	0.0	0.05	0.0	-
$n\text{C}_4\text{H}_{10}$	0.0	0.003	0.0	-
$\text{H}\cdot\text{CHO}$	0.065	) 0.62 ± 0.1	0.3 ± 0.05	0.065
CH_3CHO				
CH_3OH	0.23	0.8	1.1 ± 0.1	1.07
$\text{C}_2\text{H}_5\text{OH}$	0.05	0.6	n.d.	0.05
CH_3OOH	3.25 ± 0.3	3.5 ± 0.3	3.5 ± 0.3	3.0
$\text{G}(-\text{O}_2)$	3.42	4.51	4.2	3.6

* The propylene yield was found to increase when the ethylene concentration was increased, the results were very erratic, and only a few observations were made.

n.d. = not determined.

Section 8.10 Methane plus 0.065% Oxygen; Oxygen Consumption.

The thermistor detector is not very sensitive towards oxygen. In order to avoid product determinations involving small differences between large numbers, the concentration of oxygen had to be low, and the energy deposited in the reactants fairly high. The lower limit for the oxygen concentration has been obtained from a previous experiment, (methane plus 0.026% oxygen section 8.6 page 103) was 0.026%, and the value used was 0.065% in this study.

Irradiations were performed at 20°C and 765 mm Hg pressure, at a dose-rate of 9.32×10^{14} eV/ml/min. A dose-yield plot has been drawn, see Fig.21 page 125, from which $G(-O_2) = 6.85$.

Section 8.11 Methane plus Mercury Vapour.

Erratic product yields from the radiolysis of methane and methane plus oxygen, have on occasions been attributed to the presence of mercury in the systems (4, 46).

Irradiation of methane and methane plus oxygen have been carried out at room temperature, with mercury present, to see whether this claim is justified.

Mercury was purified by distillation, and about 0.5 g was placed in the 90 ml vessels. These vessels were then evacuated, and filled ^{with} pure methane. After dispersing the mercury round the vessel by shaking violently, irradiation

was carried out at a dose-rate of 0.4×10^{14} eV/ml/min.

The G-values of all of the products were essentially the same as obtained from the radiolysis of pure methane, except for a slight increase in $G(C_3H_8)$ and $G(i-C_4H_{10})$, see Table 12 page 115.

Section 8.12 Methane plus 2% Oxygen and Mercury Vapour.

The effect of the presence of the mercury on the peroxide and aldehyde yields was investigated. Mercury purified by distillation was dispersed in the gases as above.

The rate of formation of formaldehyde was exactly the same as that obtained from methane plus 2% oxygen, $G(H.CHO) = 0.065$. The peroxide yields were rather erratic, but an approximate value for $G(CH_3OOH)$ of 2.2 has been obtained from Fig.16 page 120. The alcohol and hydrocarbon G-values were not measured.

Section 8.13 The Mercury Sensitized Photolysis of Methane, and Methane plus 2% Oxygen.

A silica vessel of 90 ml capacity was used. The photolyses were carried out at various temperatures over the range $20^{\circ}C$ to $120^{\circ}C$. The energy deposited in the system was not measured, qualitative results only were obtained.

Hydrocarbon yields from pure methane were very low from the photolyses performed at temperatures below $45-50^{\circ}$. At $100^{\circ}C$ the ratio of ethane to propane yields decreased

from a very high figure at low conversions, to a constant value of 14 at the highest conversions. Other products noted, included hydrogen, iso-butane and normal butane, and the pentanes.

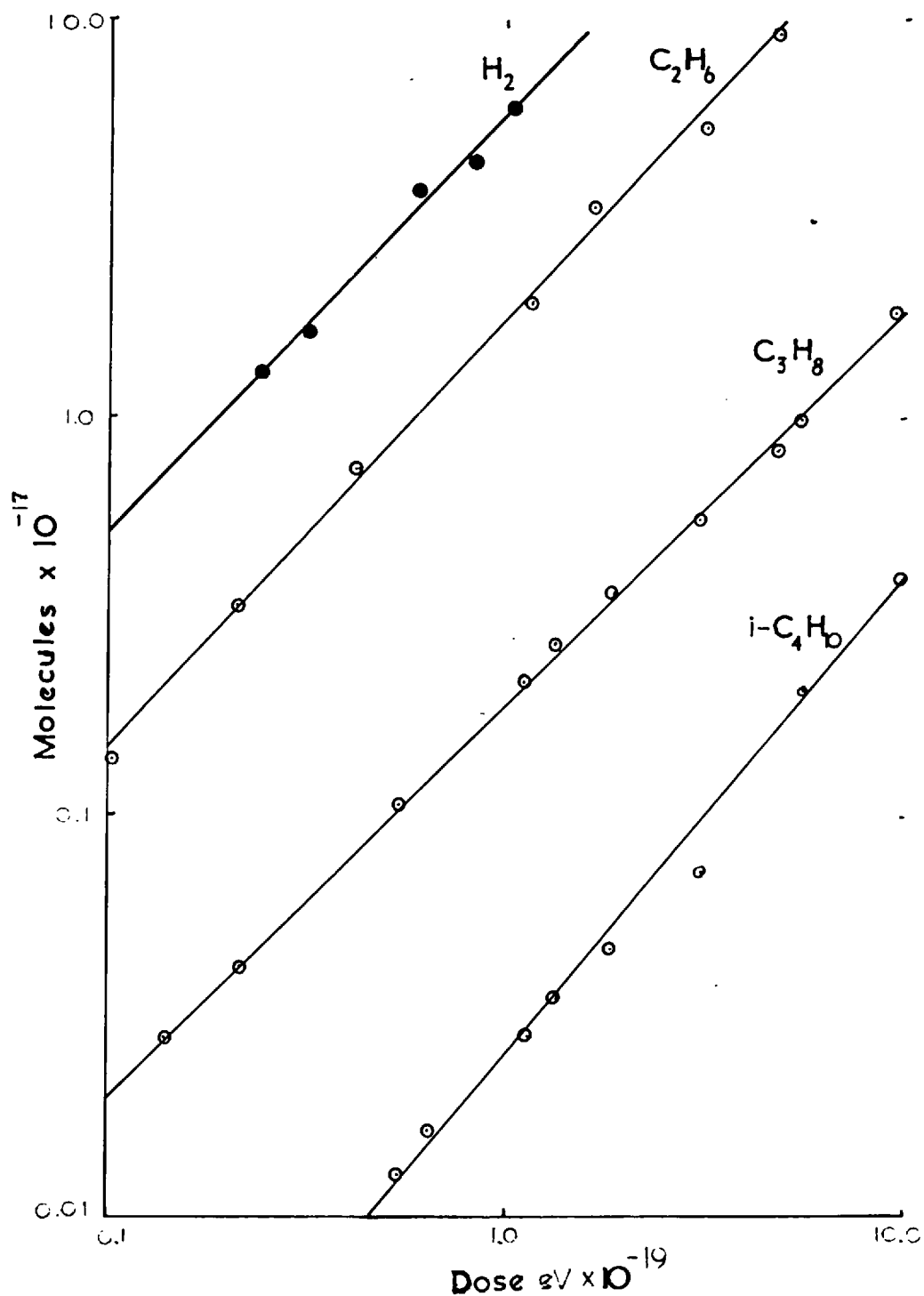
In the presence of oxygen no hydrocarbon products were observed, a small amount of hydrogen was noted. Small quantities of formaldehyde and methyl hydroperoxide were noted, the ratio of the yields was about 6:1.

Table 12.

G-values for the Products from the Radiolysis of Methane and Methane plus Mercury Vapour at 20°C.

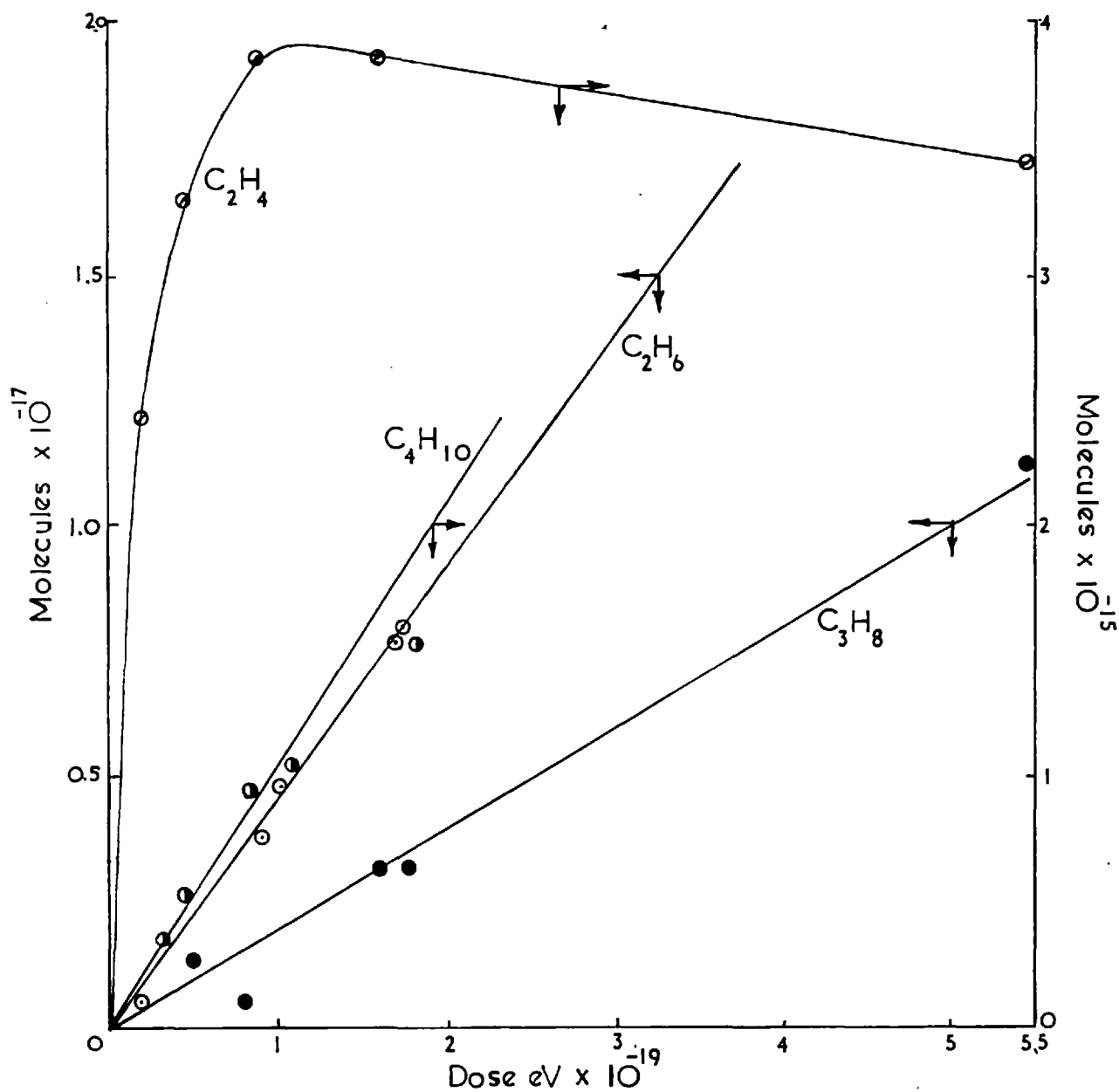
G-values

Product	Methane 20°C	Methane plus Mercury 20°C
H ₂	5.63±0.5	5.9±0.5
C ₂ H ₆	2.02±0.2	1.93±0.2
C ₃ H ₈	0.19	0.34
iC ₄ H ₁₀	0.04	0.19
nC ₄ H ₁₀	0.06	0.04



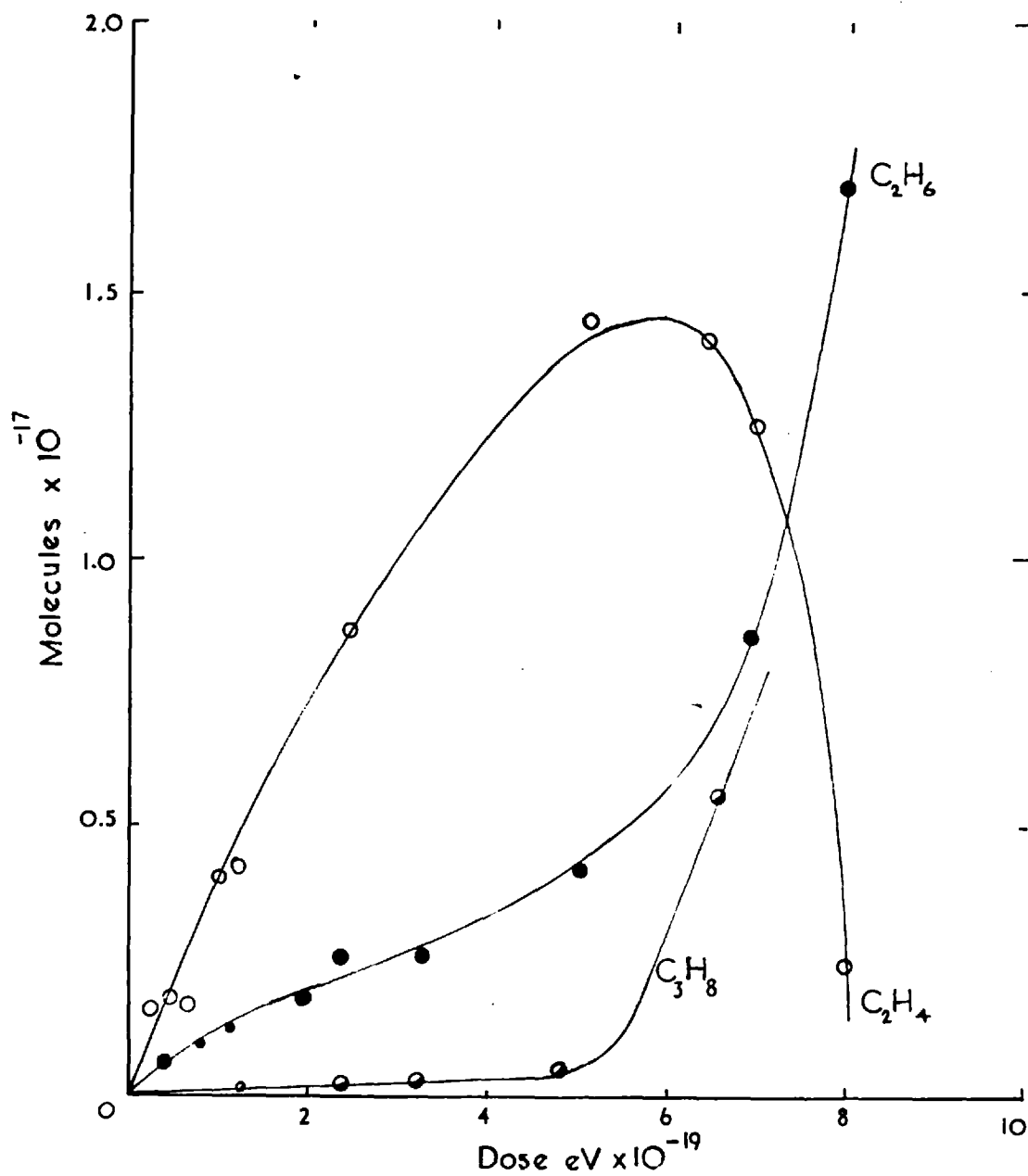
Dose-Yield plots for the major products from the radiolysis of methane at 20°C.

Fig. 12



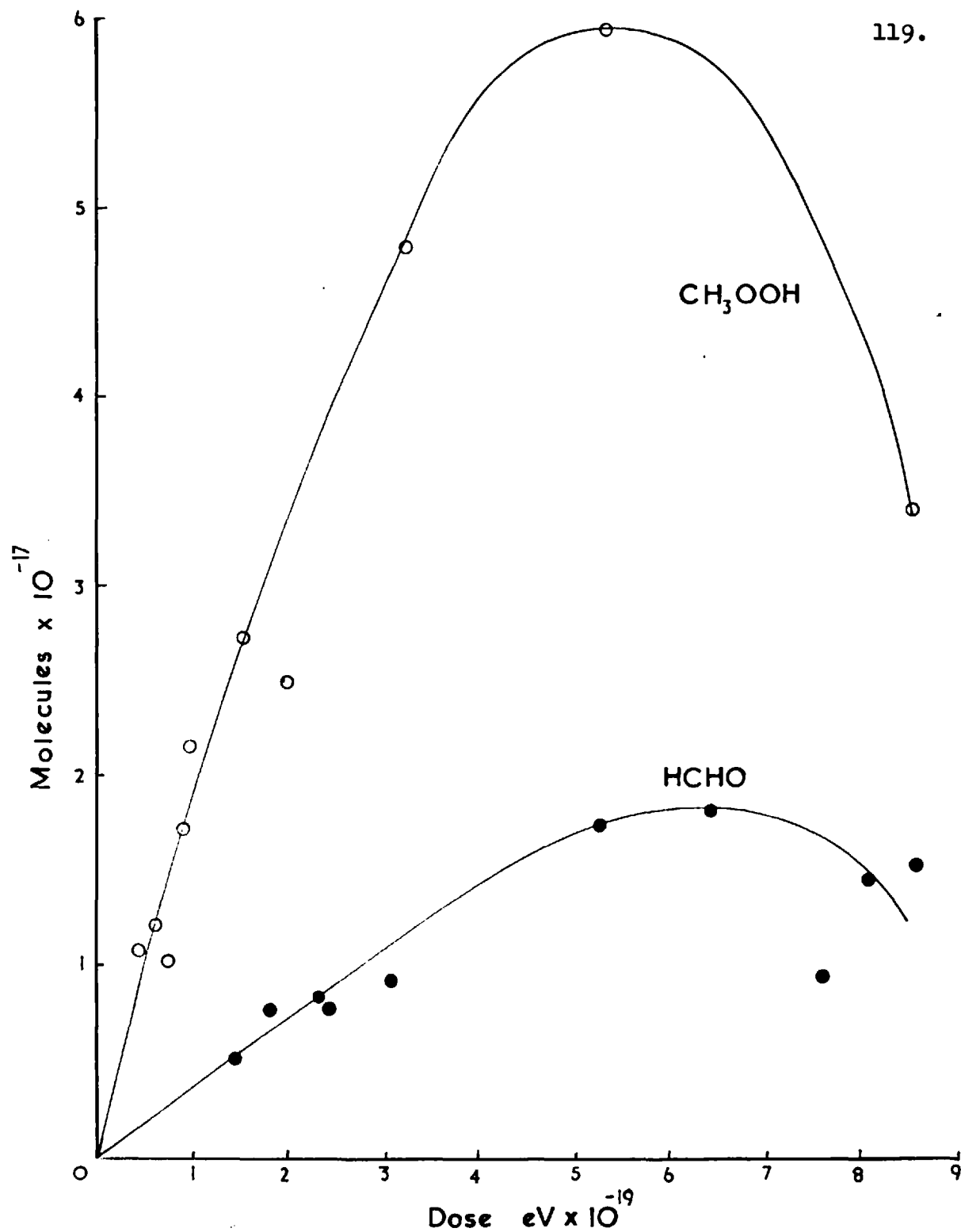
Dose-yield plots for ethane, ethylene, propane and iso-butane from the radiolysis of methane carried out at -78°C .

Fig. 13.



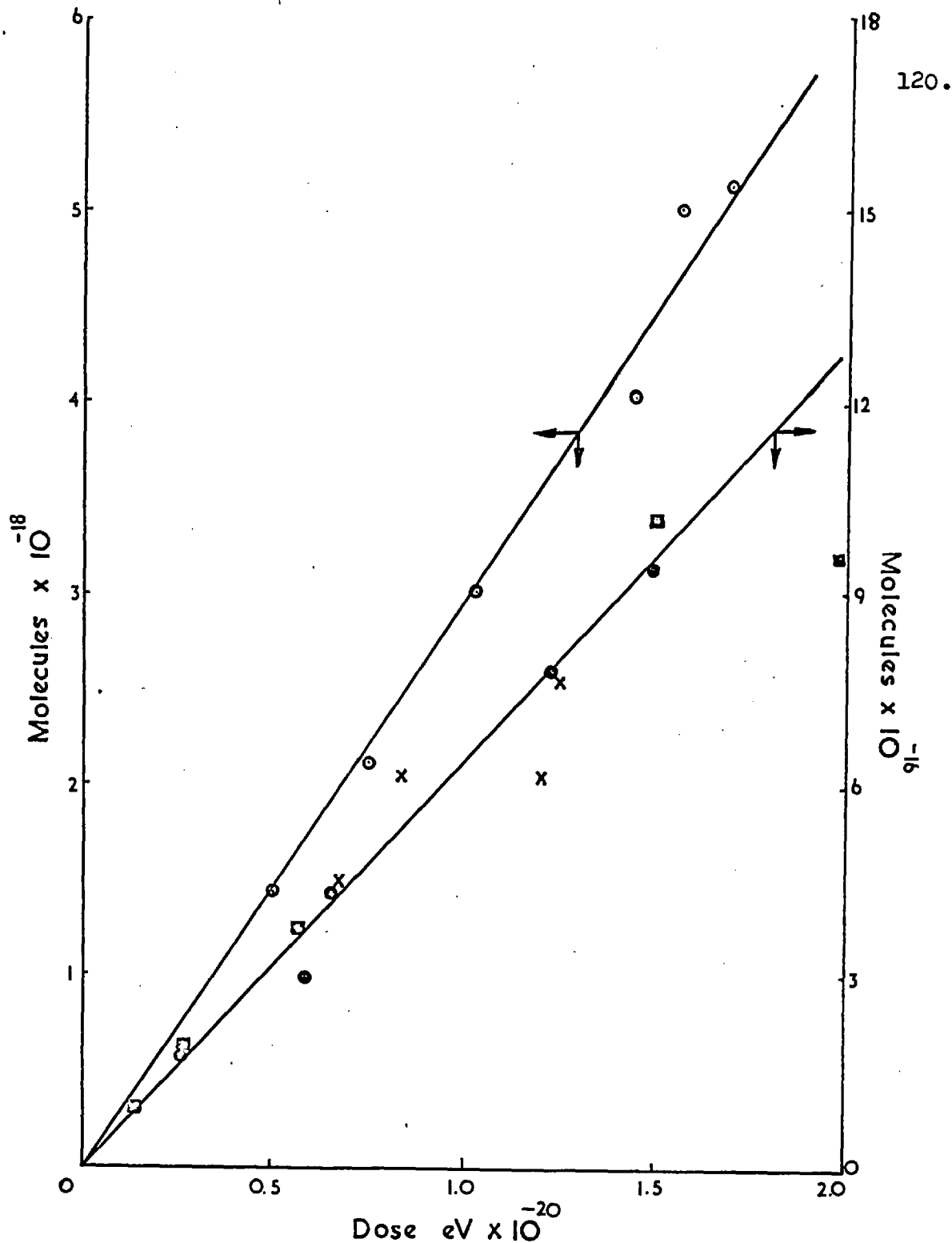
Dose-yield plots for the major hydrocarbon products from the radiolysis of methane plus 0.026 % oxygen.

Fig.14



Dose-yield plots for methylhydroperoxide and formaldehyde from the radiolysis of methane plus 0.026 % oxygen.

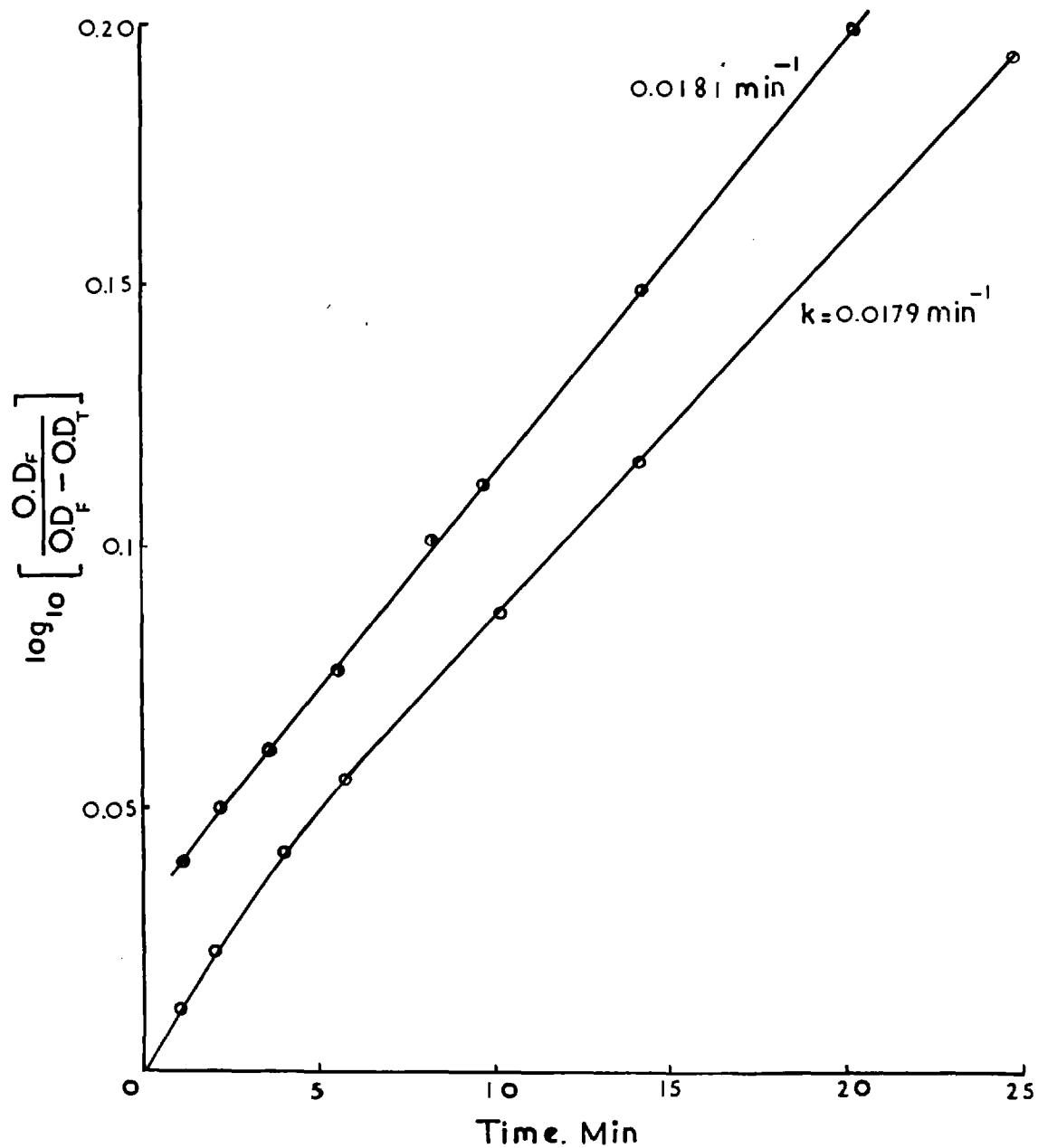
Fig.15



Dose-yield plots for methyl hydroperoxide and formaldehyde from the radiolysis of methane plus 2% oxygen in the absence and presence of mercury, at 20°C .

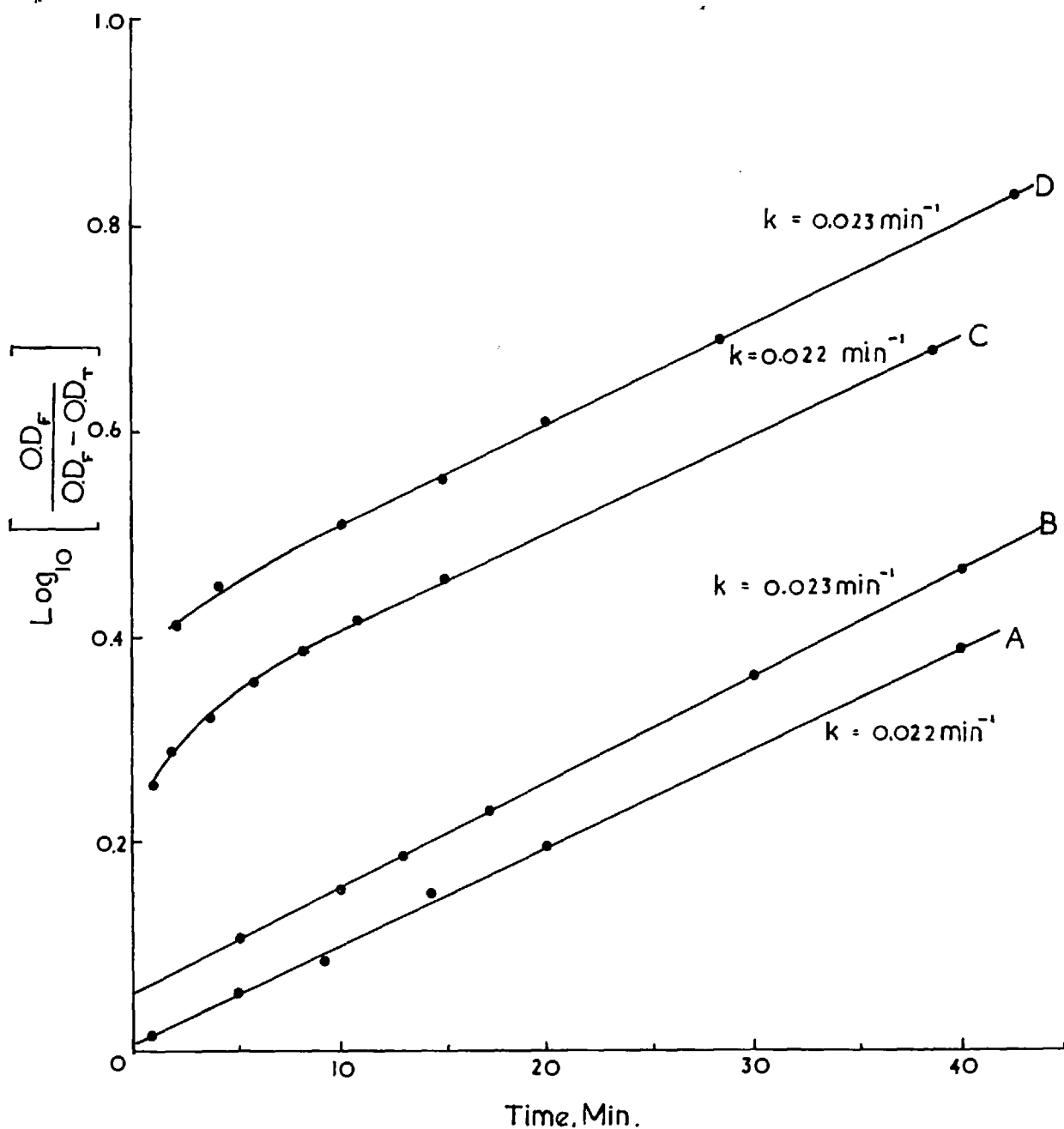
○ CH_3OOH mercury absent □ CH_3OOH mercury present.
 ● HCHO " " x HCHO " "

Fig. 16.



First order plots for the methyl hydroperoxide product from the radiolysis of methane plus 2% oxygen at 20°C.

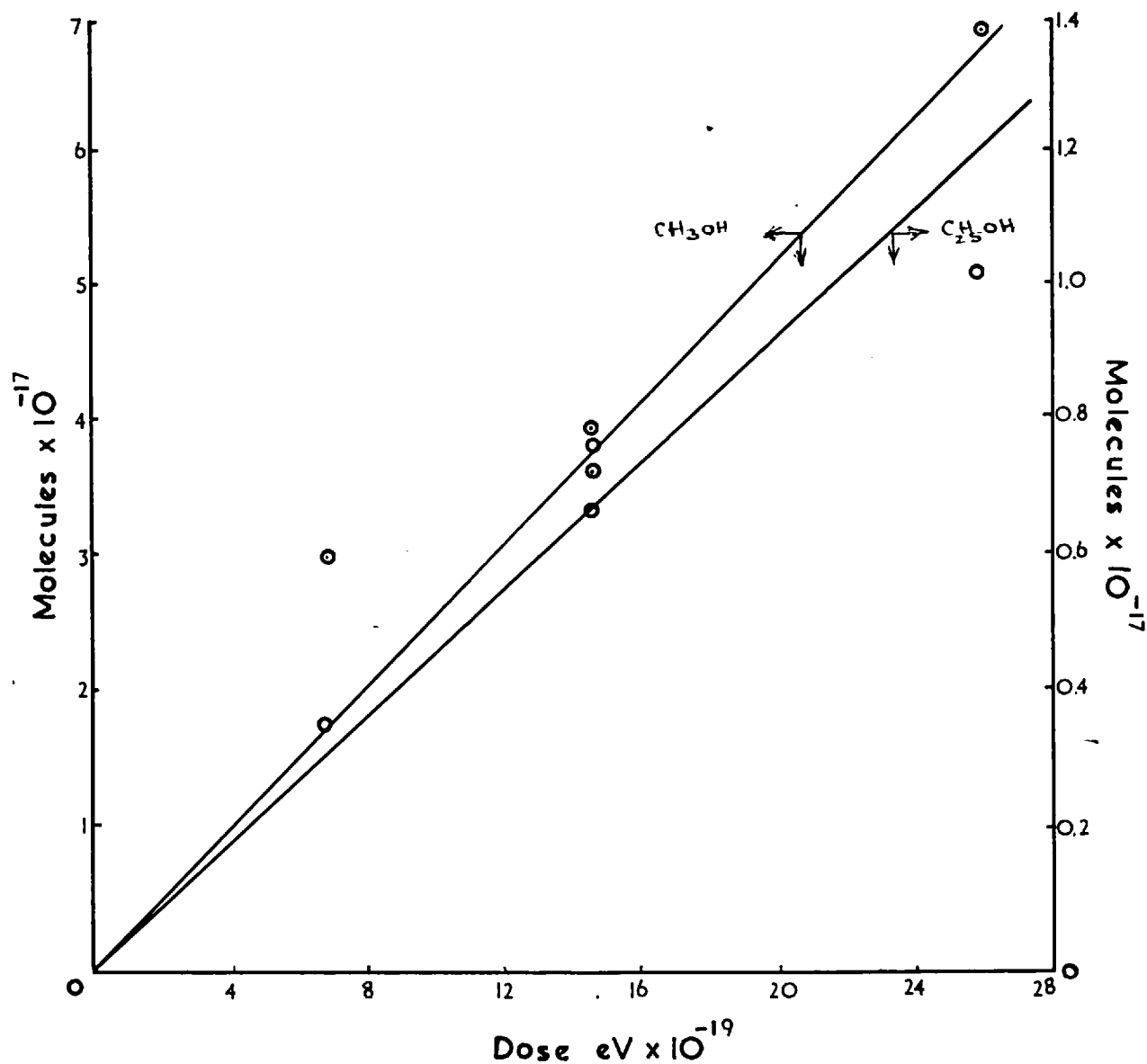
Fig.17



First order plot for the reaction between methylhydroperoxide and iodide reagent.

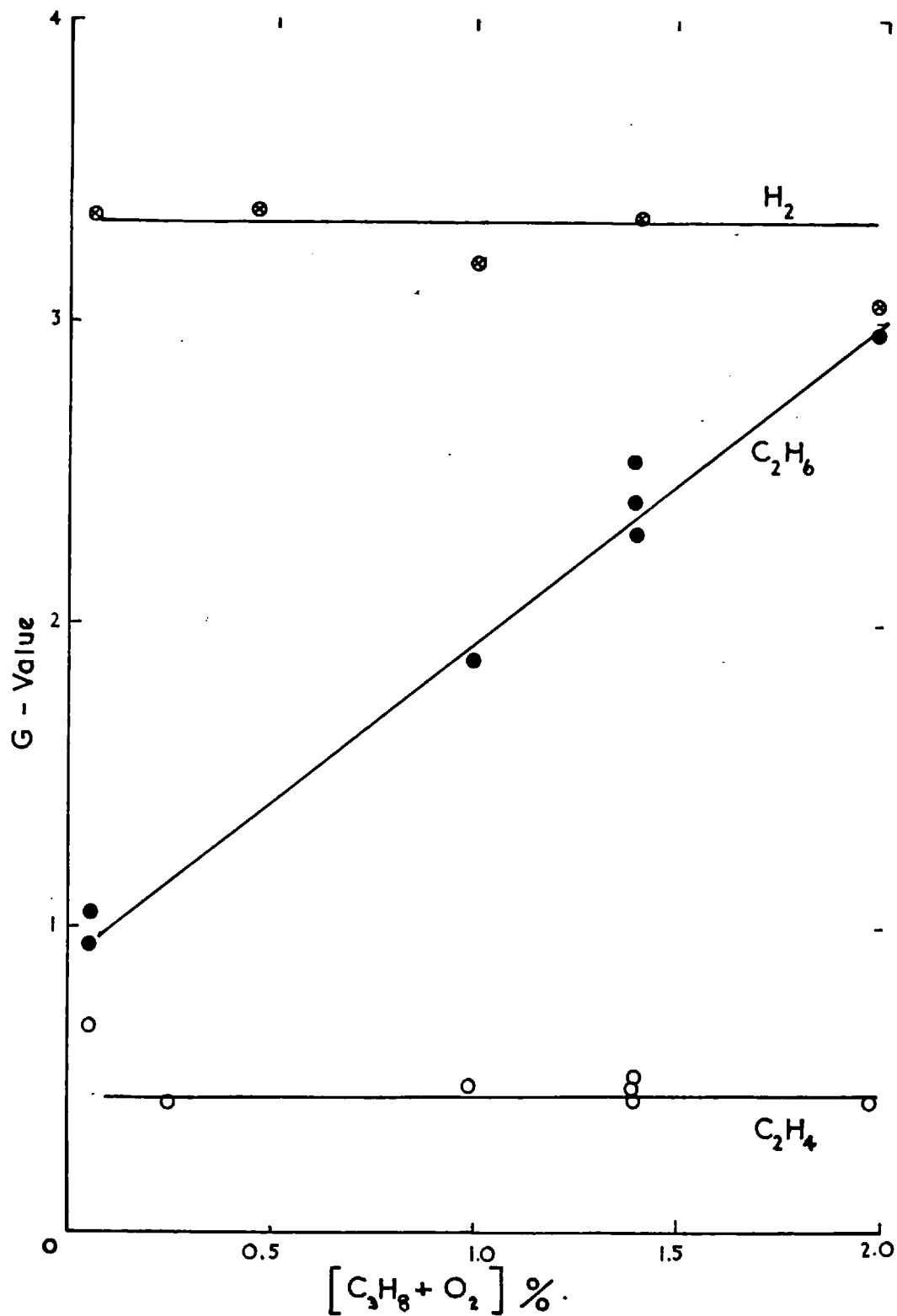
A, pure CH_3OOH . B, CH_3OOH product from $\text{CH}_4 + \text{O}_2 + \text{H}_2\text{O}$.
C and D, CH_3OOH product from $\text{CH}_4 + \text{O}_2$ irradiated at -78°C .

Fig. 18



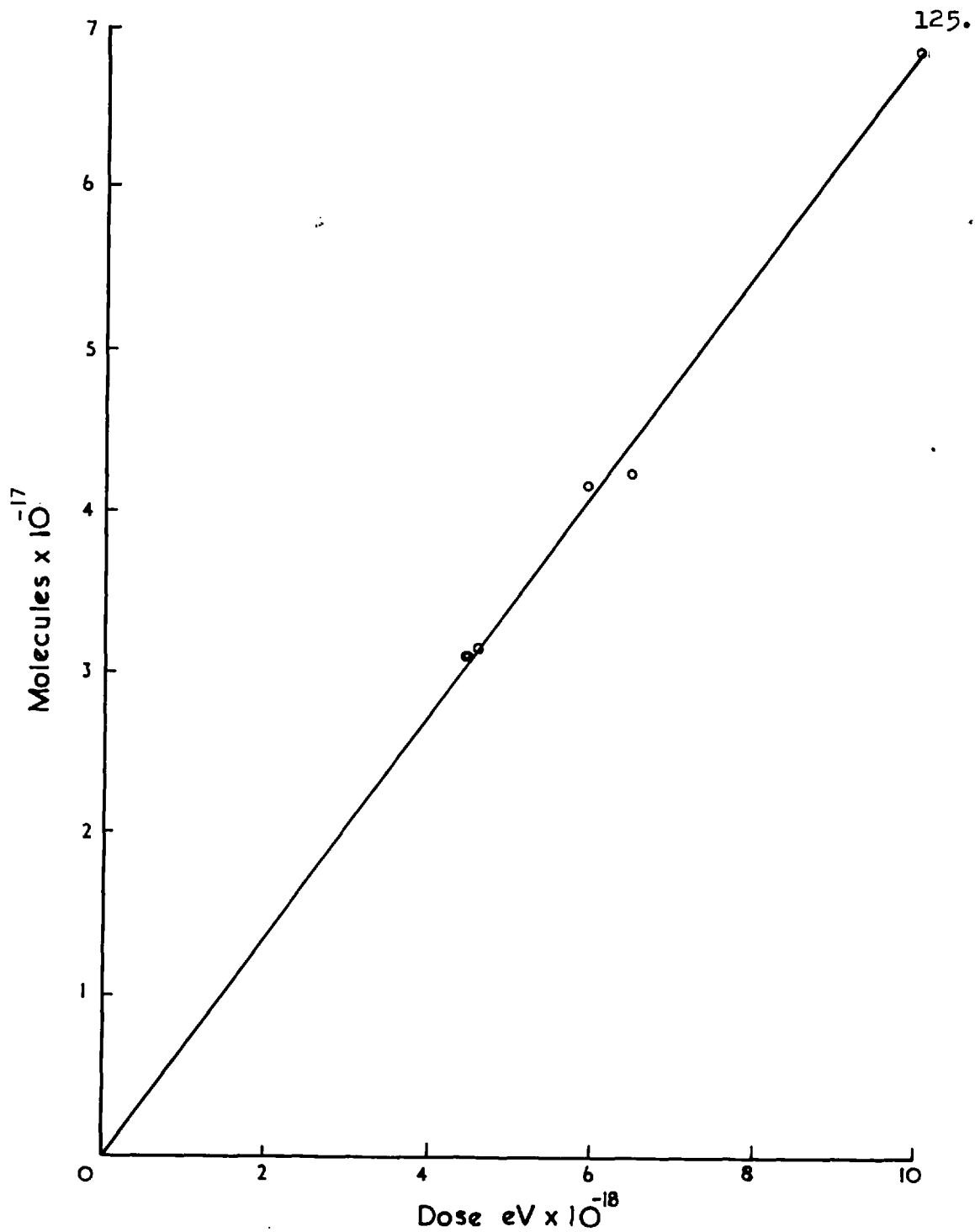
Dose-yield plots for methyl and ethyl alcohol from the radiolysis of methane plus 2% oxygen and 1% water vapour at 20°C and 765 mmHg.

Fig. 19



G-Values for the formation of Hydrogen, Ethane and Ethylene from the radiolysis of methane plus propane and oxygen against additive concentration.

Fig. 20



Oxygen consumed in the radiolysis of methane plus 0.065 % oxygen against dose received.

Fig. 21

CHAPTER IV

DISCUSSION and CONCLUSIONS.

Discussion.	Page
Section 1 Oxygenated Products.	
1.1 Oxygenated Product Formation.	127
1.2 Oxygen Consumption.	137
1.3 Effects of Mercury on Product Formation.	139
Section 2 Hydrocarbon Product Formation.	140
2.1 Methane 20°C.	140
2.2 Methane plus Ethylene.	140
2.3 Methane plus Propylene.	144
2.4 Methane plus Propylene and Water.	146
2.5 Methane plus Propane.	147
2.6 Methane plus Oxygen and Propane [Oxygen] / [Propane] = 1.	148
2.7 Methane plus Water Vapour, 0.3 and 1%.	150
2.8 Methane plus Water Vapour and Oxygen.	153
2.9 Methane plus Ethylene and Oxygen.	155
2.10 Methane plus Oxygen, 0.026 and 2%.	157
2.11 Methane plus Mercury.	161
2.12 Methane Irradiated at -78°C.	161
2.13 Polymer Formation.	164
Section 3 Conclusions.	167
3.1 Methane plus Oxygen.	167
3.2 Methane.	169
Section 4 Suggestions for Further Work.	169

DISCUSSION

Section 1.1 Oxygenated Product Formation.

The methyl hydroperoxide yield from the radiolysis of methane plus 2% oxygen at 20°C compares well with that obtained by Johnson and Salmon (45), but is 50% greater than the G-value obtained by Hummel from methane irradiated in the presence of 10% oxygen (46, 47). Although the G-value for methyl hydroperoxide formation determined from the radiolyses using 0.026% oxygen is in agreement with that noted by Hummel from methane plus 10% oxygen (46, 47), the initial G-value measured from the dose-yield plot is a minimum value and the actual figure could well be 20 to 30% greater (Fig.15 page119).

The methanol yield is about 30% less than that observed by Hummel (47) at the lower dose-rate of 2.34×10^{14} eV/ml/min. and the formaldehyde yield is a factor of about 12 less than that observed by Hummel (Table 5 page 51 and Table 10 page106). As was mentioned earlier (page 85) methyl hydroperoxide interferes when the chromotropic acid method is used to determine the formaldehyde yield, and Hummel does not seem to have taken this into account.

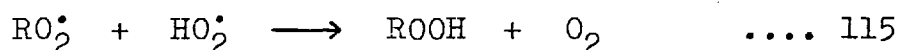
If it is assumed that the only effect of oxygen in the radiolysis of methane plus oxygen is to react with the radicals, then an estimate of the G-values for the formation of methyl radicals and hydrogen atoms may be obtained.

The decrease in $G(C_2H_6)$ on irradiating in the presence of oxygen is approximately 1.87 (Table 9 page 104) which corresponds to a $G(\dot{C}H_3)$ of 3.74. Since propane arises from reactions of methyl with ethyl radicals (38) a further number of methyl radicals equivalent to $\Delta G(C_3H_8)$, which is about 0.2 (Table 9 page 104), are present. An estimated value for $G(\dot{C}H_3)$ is therefore 3.94. Similarly $G(H\cdot)$ may be calculated. $\Delta G(H\cdot)$ is equal to $2\Delta G(H_2)$ plus the decrease in hydrocarbon products which arise from reactions in which hydrogen atoms take part. $\Delta G(H_2)$ from results obtained in the presence and absence of oxygen is 2.88. Propane and n-butane arise from reactions of ethyl radicals, which in turn are derived from the reaction of ethylene with hydrogen atoms. Hence $G(H\cdot)$ is equal to $2\Delta G(H_2) + \Delta G(C_3H_8) + 2\Delta G(nC_4H_{10})$, which is 6.26, and is in good agreement with the value of $G(H\cdot) = 6$ calculated by Hummel (20).

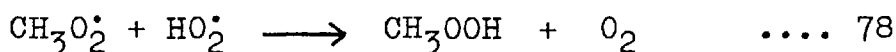
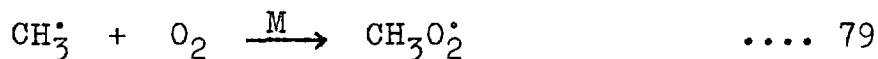
If the oxygenated products observed arise only from reactions of the hydrogen atoms, methyl radicals, and oxygen, the total yield of the various products is limited to the maximum values for $G(H\cdot)$ and $G(\dot{C}H_3)$.

The mercury photosensitised oxidation of methane (49) shows that where hydrogen atoms, methyl radicals, and oxygen are present and $G(\dot{C}H_3) = G(H\cdot)$ from reaction 4 page 18, essentially all the methyl radicals react to give methyl hydroperoxide.

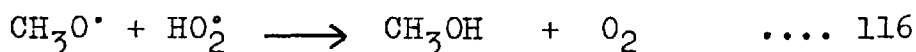
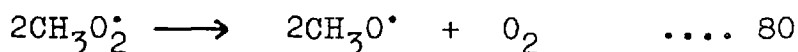
From the mercury photosensitised oxidation of ethane in the presence of excess hydrogen, Callear and Pereira (81) noted that the quantum yield of ethyl hydroperoxide was about unity, indicating that virtually all the ethyl radicals formed gave rise to the peroxide. The formation of the hydroperoxide under the above conditions has been explained on the basis of a hydrogen abstraction reaction



In the systems investigated in this work methyl hydroperoxide is considered to be formed from the methyl peroxy radical by hydrogen abstraction from the hydroperoxy radical (45).



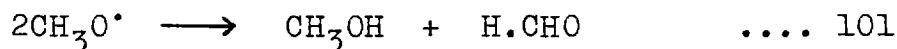
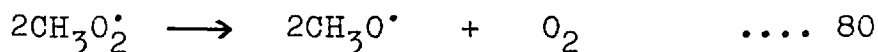
It would appear that a possible route to methanol formation is from reactions of methoxy radicals with hydroperoxy radicals.



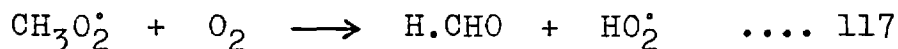
Only where no readily abstractable hydrogen is available do methyl peroxy radicals react to form methanol and formaldehyde, and generally in these systems the formaldehyde yield is equal to or greater than that of methanol.

It is difficult to see in the experiments carried out in this work why any significant quantity of methyl peroxy radicals react to give methanol rather than methyl hydroperoxide under the conditions employed.

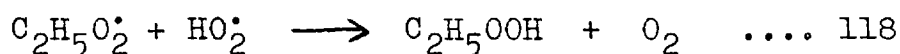
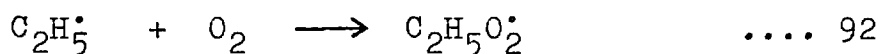
Methanol and formaldehyde can be formed from reactions of methyl peroxy radicals (61) but this does not appear to occur to any great extent since the formaldehyde yield is very low.

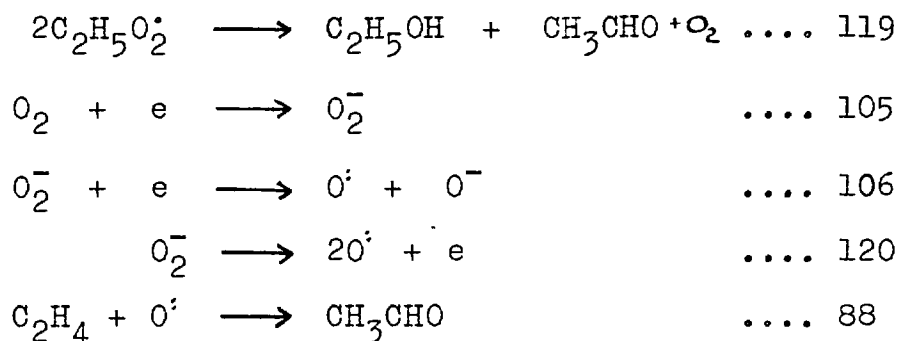


Similarly since the rate of formation of formaldehyde is so low other reactions which can give rise to formaldehyde do not occur to any significant extent.



Results from the irradiation of methane plus ethylene and oxygen can be explained on the basis that the aldehyde yield is probably mainly acetaldehyde and not formaldehyde. The acetaldehyde results from reactions of the ethyl radical (formed from the competition of ethylene with oxygen for the hydrogen atoms) with oxygen, or from ethylene plus oxygen atoms, the oxygen atoms arising from the neutralisation of O_2^- or by dissociative electron capture.





The occurrence of reaction 119 also explains why the ethyl alcohol yield is much higher than was obtained in the other systems investigated (Table 11 page 112).

The increase in the product yields (compared with those obtained from methane plus oxygen) attributed to reactions of the ethyl radical with oxygen is in relatively good agreement with the yield forecast from competition reactions of ethylene and oxygen for the hydrogen atoms, p157.

The formation of the products detected from the radiolysis of methane plus oxygen has been explained on the basis of reactions of hydrogen atoms, methyl radicals, and oxygen. From the results obtained from the various systems investigated the G-values determined experimentally can be compared with those G-values calculated for methyl radicals and hydrogen atoms (page 128). The sum of $G(\text{CH}_3\text{OOH})$, $G(\text{CH}_3\text{OH})$, and $G(\text{H}\cdot\text{CHO})$ should be equivalent to $G(\text{CH}_3^\bullet)$. Since every resulting species containing a methyl group reacts with a group containing a hydrogen atom, $G(\text{CH}_3^\bullet)$ will also represent a minimum value for $G(\text{H}^\bullet)$.

Table 13.

G-values obtained experimentally for methyl radical formation from the radiolysis of $\text{CH}_4 + \text{O}_2$, $\text{CH}_4 + \text{O}_2 + \text{C}_3\text{H}_8$ and $\text{CH}_4 + \text{O}_2 + \text{H}_2\text{O}$.

G-values

System.	$\text{G}(\text{CH}_3^\bullet)$	$\text{G}(\text{CH}_3^\bullet)$
	Experimental	Calculated
$\text{CH}_4 + 2\text{O}_2$	4.1	3.94
$\text{CH}_4 + \text{O}_2 + \text{C}_3\text{H}_8$	$\div 4.9$	"
$\text{CH}_4 + \text{O}_2 + \text{H}_2\text{O}$	3.5	"

In the presence of propane the possibility of the neutralisation of higher molecular weight ions to give amongst other species, methyl radicals makes the figure for $\text{G}(\text{CH}_3^\bullet)$ unreliable.

Only an approximate indication of the value of $\text{G}(\text{CH}_3^\bullet)$ can be obtained from Table 13, since insufficient results have been obtained. $\text{G}(\text{CH}_3^\bullet)$ is of the order of 3.5 to 4.9, and is similar to the range calculated for $\text{G}(\text{CH}_3^\bullet)$ from the decrease in the hydrocarbon product yields on adding oxygen to methane (page 128).

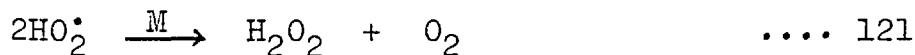
$\text{G}(\text{H}^\bullet)$ accounted for in the products measured, is similar to the value obtained from the hydrocarbon results from irradiations carried out in the presence of hydrogen atom scavengers (page 142).

The inferences from these observations are that,

- a) the rate of formation of methyl radicals is in line with that expected,

- b) that either some hydrogen cannot be accounted for, or that in the presence of oxygen and other compounds, reactions which would normally give rise to hydrogen atoms do not do so.

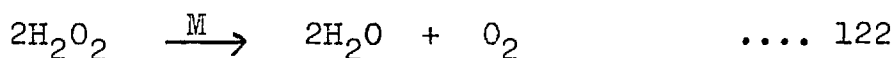
Irradiating methane at 20°C in the presence of oxygen and water, some hydrogen peroxide was found to be present as a product. The yield varied from experiment to experiment, but $G(\text{H}_2\text{O}_2)$ was of the order of 0.3. Irradiating methane plus 2% oxygen at -78°C a large yield of hydrogen peroxide was obtained. The yield was found to depend upon the surface area of the irradiation vessel used (Table 10 page 106). The smaller vessel of 312 ml capacity had a surface area of approximately 220 cm², and that of the 600 ml vessel was about 420 cm². Both vessels were irradiated at the same dose-rate and had the same surface to volume ratio. The ratio of the hydrogen peroxide to methyl hydroperoxide yields from the 312 ml vessel was about 1.5, and the ratio from the 600 ml vessel was about 3.1. These results indicate that the surface of the vessel is modifying certain reactions to give hydrogen peroxide, which at -78°C is stabilised on the walls of the vessel. Reactions of the hydroperoxy radicals, on diffusing to the walls to form hydrogen peroxide would account for the formation of this product.



Further experiments at -78°C with glass wool present in

the irradiation vessel to increase the surface area could be carried out to investigate this phenomenon.

In the presence of water, and also from irradiations carried out at -78°C , hydrogen peroxide is formed probably from hydroperoxy radicals. It is possible that it is also formed in the radiolysis of methane plus oxygen performed at 20°C , but that it readily decomposes at the walls of the vessel to give water and oxygen.



If this is so, the yield of hydrogen peroxide at 20°C would depend upon experimental and product collection conditions and would hence be erratic. The intercept at zero time of the first order plots for the total peroxide product depends upon the concentration of the hydrogen peroxide present, and would thus vary from experiment to experiment, which in fact was observed.

It might be possible to determine whether hydrogen peroxide is formed and decomposes in methane-oxygen systems irradiated at 20°C , by irradiating at -78°C , allowing the vessel to warm up to 20°C and then re-irradiating at this temperature. The change in the hydrogen peroxide concentration would indicate whether or not decomposition occurs in the systems irradiated at 20°C .

In the radiolysis of methane plus oxygen, if excess hydrogen atoms react eventually to appear in water,

$G(H_2O)$ could be as high as 1 since $G(H\cdot)$ unaccounted for is about 1.5 to 2 (page 168).

The free methyl radicals and hydrogen atoms available at $-78^\circ C$ can be determined as was done previously for the radiolyses at $20^\circ C$. $\Delta G(CH_3\cdot)$ is 0.6, and $\Delta G(H\cdot)$ is 1.5, from the decrease in the yields of ethane and hydrogen respectively in the presence and absence of oxygen (Table 9 page 104). The maximum value for $G(CH_3OOH) + G(CH_3OH) + G(H\cdot CHO)$ is therefore 0.6. In fact from the yields for these products from the larger vessel, $G(CH_3\cdot) = 2.2$ and $G(H\cdot) = 8.4$. These figures are completely at variance with values expected from $\Delta G(C_2H_6)$ and $\Delta G(H_2)$. Until further studies have been performed to determine $G(CH_3\cdot)$ and $G(H\cdot)$ more accurately at $-78^\circ C$, no explanation of these results can be put forward.

Hummel has measured the yields of the products from methane plus 10% oxygen, having G-values of formation as low as 0.002 (47). Some of the products contain the ethyl group and can presumably be derived from reactions of the ethyl radical or the ethyl ion. The ratio of oxygen concentration to hydrocarbon ion scavenger concentration (the hydrocarbon products) is sufficiently high for oxygen to react with the ions. The sum of the G-values of the products obtained by Hummel from methane plus 10% oxygen which contain the ethyl group is 0.42, which is equal to the value for $G(C_2H_5^+)$ found in this work (page 147).

It therefore appears that oxygen reacts with the ethyl ion, since the formation of the ethyl radicals in this system is hard to explain. As mentioned above, where ethyl radicals are present as in the radiolysis of methane plus oxygen and ethylene, ethanol (and probably acetaldehyde) is found present suggesting that these products arise from reactions between ethyl radicals and oxygen.

The effects of the removal of the major ions CH_5^+ and C_2H_5^+ on the formation of the products from methane plus 2% oxygen were investigated by adding propane and water to the systems prior to radiolysis. Results from the radiolysis of methane plus oxygen and propane ($\text{O}_2/\text{C}_3\text{H}_8 = 5$ and $\text{O}_2 + \text{C}_3\text{H}_8 = 2\%$) show that there is little change in the oxygenated product distribution (Table 11 page 112). The ratio of oxygen to propane is less than that required for oxygen to compete with propane for the removal of CH_5^+ or C_2H_5^+ (24, 26) and these ions will react with the propane. Since the rate of formation of the major products remains essentially the same as was obtained from methane plus 2% oxygen, neither of these ions can play any part in the formation of methyl hydroperoxide or methanol.

In the presence of water the methanol yield decreased to approximately one quarter of that obtained in the absence of water. The methyl hydroperoxide yield was virtually unaffected. (Table 11 page 112).

The evidence from the experiments involving the use of ion scavengers for formation of methanol is rather conflicting. Water very efficiently removes the ions CH_5^+ and C_2H_5^+ , and it is not certain therefore that CH_5^+ does not play any part in the formation of methanol.

Section 1.2 Oxygen Consumption.

The decrease in the concentration of the oxygen additive is linear with increasing dose (Fig.21 page 125), and from the slope of the plot $G(-\text{O}_2)$ is 6.85. An approximate G-value for oxygen consumption can be calculated from results of the radiolyses in which the oxygen concentration was 0.026%. The dose at which the oxygen is almost completely consumed may be obtained from Figs.14 and 15 pp.118-9; the initial concentration of the additive is known, and $G(-\text{O}_2)$ at that point may be determined. The value thus determined is only approximate since the exact dose at which there is no oxygen present is not known, and the mixtures were made up on a pressure basis using the Pirani gauge (which is not very accurate). The $G(-\text{O}_2)$ so obtained is about 8. The value from the slope of the dose-yield plot is of the same order as the figures calculated for the oxygen appearing in the products obtained by Hummel (47) and Mikhailov (44), at high dose-rates of the order of 10^{18} eV/ml/min.

At a dose-rate of 2.34×10^{14} eV/ml/min, Hummel (47) obtained lower yields for most of the major oxygenated

products, and $G(-O_2)$ calculated from the products is approximately 3.8. This is virtually the same as has been found in this work for methane plus 2% oxygen, in the presence and absence of water (Table 11 page 112), and shows that about half of the oxygen consumed is unaccounted for. There is good agreement between $G(-O_2)$ obtained here where only $G(CH_3OOH)$, $G(CH_3OH)$, and $G(H.CHO)$ were measured, and the value obtained from Hummel's experiments where the yields of the products having G-values as low as 0.002 were determined.

$G(-O_2)$ for the oxygen appearing in the products from methane plus oxygen irradiated at $-78^\circ C$ is about 5. Since large amounts of hydrogen peroxide are found present as a product, this could mean that it is also formed in the radiolyses carried out at $20^\circ C$. The hydrogen peroxide formed at $20^\circ C$ (as was mentioned above) probably decomposes readily giving water and oxygen, thus contributing to the oxygen consumption.

In addition to oxygen in the water formed during radiolysis, oxygen would be present in carbon dioxide, carbon monoxide, and formic acid, which may be products at low doses. The G-values for these products obtained by Mikhailov et al. (44) are undoubtedly not initial G-values the conversions being very high. Hummel calculated that $G(H.COOH)$ was equal to or greater than 0.13 at a dose of 7×10^{17} eV/ml/min, and equal to or

greater than 0.5 at a dose of 4×10^{18} eV/ml (47). Formic acid (and possibly carbon dioxide and carbon monoxide) therefore probably arises largely from the degradation of initial products by radiation and radical attack.

Section 1.3 Effects of mercury on product formation.

The effect of mercury on the yields of formaldehyde and methyl hydroperoxide was found to be less pronounced than was expected (page 114). Gray also found that mercury had little effect on the yield of methyl hydroperoxide (49), as only very small amounts of formaldehyde were formed by reaction between methyl hydroperoxide and mercury. The effect of mercury on the products from the radiolysis of methane plus 10% oxygen was investigated by Hummel (47) at room temperature and at about 100°C. Methyl hydroperoxide was considered to decompose to yield methanol and possibly large amounts of formaldehyde, the temperature having little effect on the decomposition.

From results obtained in this work the methyl hydroperoxide yield was reduced by about 30% but the formaldehyde yield did not change. The methanol yield was not determined. It was believed at one stage (4, 47) that the irreproducibility in the product yields was due to the presence of mercury vapour. The above observations show that in the presence of large quantities of mercury the product yields are only slightly affected. Hence trace amounts of mercury would be unlikely to have any

appreciable effect on the product yields (Table 12 page 115).

The mercury photosensitised oxidations carried out at about 100°C showed that the decomposition of the major oxygenated compounds was high at this temperature. The ratio of formaldehyde to methyl hydroperoxide yields was about 6 to 1. Thus at 100°C methyl hydroperoxide is probably the only oxygenated product formed (only trace amounts of methanol were found present), and decomposition of this peroxide results in the formation of formaldehyde. This is in accord with results obtained by Gray (49), and the observations of Callear and Pereira (81) who obtained ethyl hydroperoxide in a quantum yield of unity from the mercury photosensitised oxidation of ethane in the presence of excess hydrogen.

Section 2. Hydrocarbon Product Formation.

Section 2.1 Methane 20°C.

The product yields are similar to those obtained by other workers; see Table 14 (page 144). At very low doses of the order of 5×10^{15} eV/ml, ethylene was obtained as a product, in small yield. $G(C_2H_4)$ was approximately 0.12 and is less than the value of 0.3 obtained by Hummel (20). No acetylene was noted.

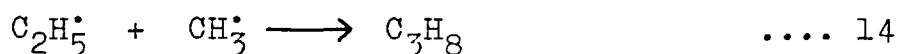
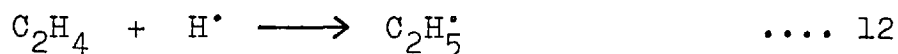
Section 2.2 Methane plus Ethylene.

Methane has been irradiated in the presence of ethylene by several workers (16, 20, 23, 82). The product

yields obtained vary considerably (Table 14 page 144). It was decided that further work was justified to attempt to resolve the disparity between the results obtained.

The product yields were found to be independent of the ethylene concentration over the range 0.3 to 2% and except for ethane and iso-butane, are much lower than those obtained by Hummel (20). The dose-rate used by Hummel was about 10^3 times greater than that used in this work. It is difficult to make comparisons with the results of Sieck and Johnsen (16), as they found that all the product yields varied with additive concentration.

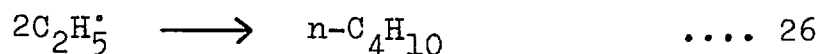
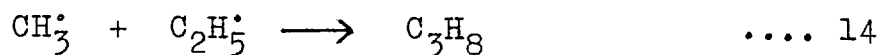
Presumably the main effect of the ethylene is to scavenge hydrogen atoms, giving rise to ethyl radicals. This work shows that since the rate of hydrogen formation is the same at 0.3% ethylene as at 2%, ethylene effectively removes the hydrogen atoms even at low additive concentrations. Results obtained by Hauser (38) indicate that the ethylene formed in the radiolysis of methane reacts with hydrogen atoms to form ethyl radicals. Using labelled ethylene $C_2^1H_4$ as an additive Hauser showed that a large part of the propane formed, on irradiating methane plus a small concentration of the additive, contained labelled carbon. It was concluded that the propane arose from reactions of the ethyl and methyl radicals.



Sieck and Johnsen (16) consider that the ethyl radical reacts further with hydrogen atoms to give ethane. Kinetic considerations show that at the concentrations of ethylene employed in this work, all of the hydrogen atoms will react with the ethylene present to form ethyl radicals. $[C_2H_5^\bullet] / [C_2H_4]$ is of the order of 10^{-8} and k_{12} is 6×10^{-11} cc/molec/sec (47), and k for the reaction between $C_2H_5^\bullet$ and $H^\bullet$ is $\sim 10^{-11}$ cc/molec/sec. (40).

The effect of the radiation on methane is to produce the same intermediate species no matter what the concentration of the additive is over a large range. Thus product yields should reach constant values and be independent of the additive concentration, if the only effect of the ethylene is to react with the species formed from methane. The results of Sieck and Johnsen (16) and Hamling et al. (82) indicate that at the higher additive concentrations used, reactions other than $C_2H_4 + H^\bullet \longrightarrow C_2H_5^\bullet$ must be occurring.

The decrease in $G(H_2)$ brought about by the addition of ethylene is 2.63, which represents a $G(H^\bullet)$ of 5.26. If propane and normal-butane are formed by reactions 12, 14, and 26, then 3.7 hydrogen atoms can be accounted for. The rest of the hydrogen atoms may possibly be present in higher hydrocarbon products (C_5 etc.) not measured.



Assuming that reaction 14 gives rise to the propane product, the drop in the ethane yield from the loss of methyl radicals which would otherwise give rise to ethane is half of the propane yield, namely $\Delta G(C_2H_6) = \frac{1}{2} \times 1.3 = 0.65$. This is in accord with the measured $\Delta G(C_2H_6) = 0.76$ (Table 14 page 144).

There would appear to be a discrepancy in Hummel's values for $G(C_2H_6)$, $G(C_3H_8)$ and $G(C_4H_{10})$ obtained in the presence of ethylene. Hummel did not measure $G(H_2)$ but states that $G(H\cdot)$ from $G(C_3H_8)$ plus $2G(nc_4H_{10})$ is 6. This is about 20% greater than the value of 5.26 obtained in this work. From Hummel's results $\Delta G(C_2H_6)$ in the presence and absence of ethylene is 0.5, which corresponds to $\Delta G(\dot{C}H_3) = 1$. Since $G(C_3H_8)$ is 2 and $G(ic_4H_{10}) = 0.1$, $\Delta G(\dot{C}H_3)$ is 2.1 and there are therefore more methyl radicals present in the products than are available from the decrease in $G(C_2H_6)$.

Although methylene radicals would be expected to react readily with ethylene to give propylene (83), no propylene was found present. It is interesting to note that in the presence of oxygen, propylene was found as a product with a G-value of formation of 0.25. This suggests that propylene formed in the presence of oxygen is protected from further reactions by oxygen.

Table 14.

G-values for Hydrogen and the Hydrocarbon
Products from the Radiolysis of CH₄,

CH₄ + C₂H₄, and CH₄ + C₃H₆.

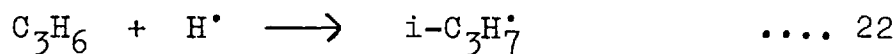
G-values

System.	CH ₄		CH ₄ + 1% C ₂ H ₄			CH ₄ + 1% C ₃ H ₆	
	T	W (20)	T	W (16)	(20)	T	W (20)
Product.							
H ₂	5.63	5.6	3.0	5.2	-	2.7	-
C ₂ H ₂	0.0	0.3	-		0.19	-	0.13
C ₂ H ₄	0.12	0.3	-	-	-	1.34	1.4
C ₂ H ₆	2.02	2.0	1.26	2.8	1.5	0.9	1.34
C ₃ H ₆	0.0	0.0	-		0.0	-	-
C ₃ H ₈	0.19	0.35	1.31	0.5	2.0	1.09	1.2
iC ₄ H ₁₀	0.04	0.08	0.12	-	0.1	0.83	2.03
nC ₄ H ₁₀	0.06	0.15	1.12	0.2	2.0	0.07	0.08

TW = This Work.

Section 2.3 Methane plus Propylene.

The principal reaction of the additive is to scavenge hydrogen atoms to form the iso-propyl radical.

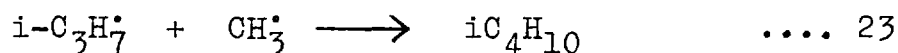


The product yields (except for iso-butane which is about 60% less) at 1% propylene concentration, are similar to those obtained by Hummel (20) Table 14 above. The dose-rate used by Hummel was about 10³ times greater than

that used in this work.

The propane and iso-butane yields are independent of the additive concentration over the range 0.01 to 1% studied. The rate of formation of ethane decreases as the additive concentration is increased from 0.01 to 1%.

At the lower additive concentration it was possible to make an approximate estimate of $G(-C_3H_6)$, since about half of the additive was consumed during the radiolysis. Propylene removes hydrogen atoms by reaction 22 and at the lower concentration the ethylene product possibly competes for the hydrogen atoms. The iso-butane arises from reactions of the iso-propyl radical with methyl radicals.

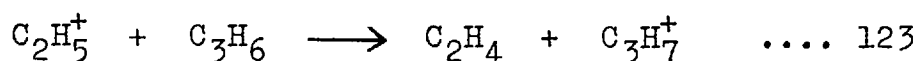


The mechanism of product formation is not clear, and only a minimum value for hydrogen atoms appearing in the products can be obtained from $G(-C_3H_6)$, from which $G(H^{\bullet}) = 2.5$. Higher hydrocarbons (C_5 and greater) were not measured and these compounds probably account for some of the hydrogen atoms. A recent report (82) indicates that the C_5 and higher hydrocarbons may well be present in reasonably large amounts. That the hydrogen yield is the same at both additive concentrations shows that propylene readily scavenges the hydrogen atoms formed.

Using 1% of the additive the decrease in $G(C_2H_6)$ compared with that obtained from methane, can to some extent be accounted for in terms of methyl radicals

reacting to give propane and iso-butane instead of ethane. $\Delta G(C_2H_6) = 1.1$ which corresponds to $\Delta G(CH_3\dot{C})$ of 2.2, and the methyl radicals appearing in the products is equal to $\Delta G(C_3H_8) + \Delta G(iC_4H_{10}) = 1.7$.

It is not possible to say at present exactly why $G(C_2H_6)$ and $G(C_2H_4)$ change with increasing propylene concentration, and yet $G(C_3H_8)$ and $G(iC_4H_{10})$ do not alter. It is possible that the ethane is formed by processes which do not depend upon reactions of methyl radicals, and that there is no change in the rate of formation of the latter with additive concentration. The formation of ethylene may be related to reactions of the ethyl ion with propylene.



Section 2.4 Methane plus 2% Propylene and Water Vapour.

Except for the iso-butane yield, the yields of the other hydrocarbon products measured are less than those obtained when the irradiations were performed in the absence of water vapour. That the G-value for iso-butane formation does not alter is probably due to its being formed by a radical process, as has been discussed in section 2.3 above.

Water would be expected to remove ethyl ions, to form ethylene, which would then not be available for ethane formation, reactions 113 and 54. The decrease in

$G(C_2H_6)$ compared with that obtained from the radiolysis of methane plus 1% propylene is 0.45, which indicates that $G(C_2H_5^+)$ is 0.45. There is however no corresponding increase in $G(C_2H_4)$, in fact the G-value for ethylene formation decreased from 1.34 to 0.8.

The mechanism of product formation is complicated by the possible reactions between ions with water and propylene. Propylene reacts with hydroxyl radicals, which also react with methane to form methyl radicals. The hydroxyl radicals could be formed by dissociative electron capture by the ion H_3O^+ (85). Since the ethane yield is small it is doubtful that the hydroxyl radicals if they are present, react with methane to give methyl radicals. However this is not certain, since the hydroxyl radicals may not be present in sufficient quantities to have any appreciable effect, and propylene competes for their removal. The H_3O^+ may also be neutralised to form hydrogen atoms and water and not give rise to hydroxyl radicals at all (86).

Section 2.5 Methane plus Propane.

The presence of 0.01% propane caused virtually no change in the product distribution or yields. There was a slight increase in the butane yield. The propane formed during the radiolysis, $G(C_3H_8) = 0.3$, is in fair agreement with the values obtained from the radiolysis of methane (Table 14 page 144). The G-value for ethane

formation is in agreement with that obtained by Ausloos (24) from the radiolysis of methane plus 0.01% propane, and tends to confirm his hypothesis that even in the absence of added propane the ethyl ion (and possibly CH_5^+) react to give ethane. The small decrease in $G(\text{H}_2)$ is within the limits of the experimental error.

Increasing the propane concentration to 1% causes a large increase in $G(\text{C}_2\text{H}_6)$, from 2.3 to 4.6. At present no explanation of this observation is available. The purity of the gas mixture was repeatedly checked and the large ethane yield was not due to its being present initially as an impurity.

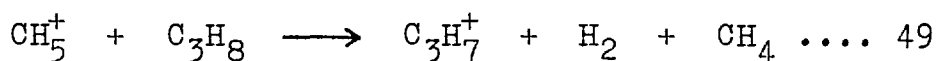
The results obtained at both additive concentrations represent product yields at low doses, but are possibly not initial yields since insufficient results were obtained for dose-yield plots to be drawn.

Section 2.6 Methane plus Oxygen and Propane, $\frac{[\text{Oxygen}]}{[\text{Propane}]} = 1$.

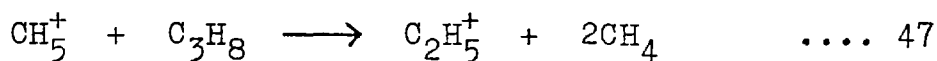
Propane should efficiently remove the CH_5^+ and C_2H_5^+ ions at all concentrations, but in the presence of oxygen, competition for these ions may occur as suggested by Ausloos (24).

G-values obtained for product formation confirm Ausloos' results where the experimental conditions overlap. $G(\text{H}_2)$ and $G(\text{C}_2\text{H}_4)$ were found to be 3.34 and 0.42 respectively and were independent of the percentage of the additives

present (Fig.20 page 124). $G(C_2H_6)$ increased with increasing additives concentration (Fig.20 page 124), which is in agreement with the general trend of Ausloos' results. $G(C_2H_6)$ increased from about 1 at 0.01% $C_3H_8 + O_2$, to 3 at 2% $C_3H_8 + O_2$. In the presence of oxygen ethane cannot arise from radical reactions and the increase in $G(C_2H_6)$ can only be the result of ionic reactions. Under the conditions of the experiment, $[O_2]/[C_3H_8] = 1$, $G(C_2H_6)$ should equal $G(C_2H_5^+) + G(CH_5^+)$ on the mechanism proposed by Ausloos (24), since oxygen only scavenges radicals and not ions when O_2/C_3H_8 is less than about 10 (24, 26). Munson (27) suggests that CH_5^+ may undergo dissociative proton transfer with propane,

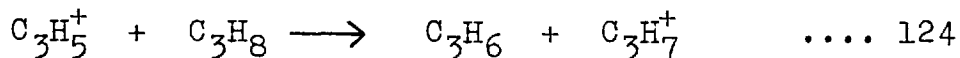


hence the full yield of $C_2H_5^+$ would not be obtained (reaction 47)



This however does not explain why $G(C_2H_6)$ increases with increasing concentration of the additives. The increase in $G(C_2H_6)$ is probably related to the similar increase in the absence of oxygen, and no satisfactory explanation can currently be suggested for this observation.

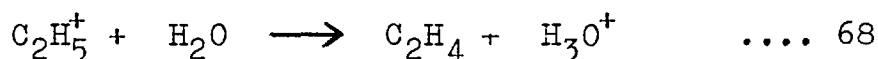
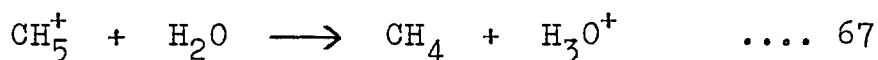
The small amount of propylene formed may arise from the $C_3H_5^+$ ion reacting with propane (82).



$C_3H_5^+$ is derived from CH_2^+ (reactions 31 and 37), which has a G-value of between 0.2 and 0.3, which compares well with $G(C_3H_6) = 0.25$ obtained in this work.

Section 2.7 Methane plus Water Vapour, 0.3% and 1%.

Work by Munson (15) showed that water very effectively scavenges the major secondary ions from methane. Reactions were proposed between the ions CH_5^+ and $C_2H_5^+$ and water leading to H_3O^+ by ~~hydride~~^{proton} ion transfer.



The product yields observed in this experiment are the same at both water concentrations used. No ethylene was found to be present, but it is to be expected that reaction with hydrogen atoms would readily remove this product. The resulting ethyl radicals would give rise to increases in the propane and n-butane yields. This does in fact occur (Table 15 page 151), but the increases in the G-values are small, $\Delta G(C_3H_8) = 0.2$ and $\Delta G(nC_4H_{10}) = 0.1$. These figures correspond to an ethylene yield equivalent to $G(C_2H_4)$ of about 0.4, which is somewhat lower than the value proposed for $G(C_2H_5^+)$ by Ausloos, namely 0.9 (24).

Table 15.

G-values for Hydrogen and the Major Hydrocarbon Products from the Radiolysis of Methane, Methane plus Water, and Methane plus Oxygen and Water.

G-values

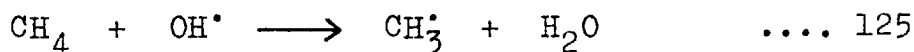
System.	CH ₄	CH ₄ + H ₂ O	CH ₄ + O ₂ + H ₂ O
Product.			
H ₂	5.63 ± 0.5	6.1 ± 0.5	2.7 ± 0.2
C ₂ H ₄	0.12	0.0	0.85 ± 0.05
C ₂ H ₆	2.02 ± 0.2	1.53 ± 0.12	0.155 ± 0.01
C ₃ H ₈	0.19	0.37 ± 0.04	0.0
iC ₄ H ₁₀	0.04	0.08	0.0
nC ₄ H ₁₀	0.06	0.15	0.0

The decrease in the ethane yield should be related to $G(C_2H_5^+)$ and $G(CH_5^+)$ since these ions give rise to ethane under normal conditions in methane radiolysis (24). Furthermore removal of the ethyl ion gives ethylene which reacts with hydrogen atoms to form ethyl radicals, and these radicals react with methyl radicals to form propane. The removal of some methyl radicals by $C_2H_5^\bullet$ thus decreases the ethane yield still further. A maximum value for $G(C_2H_6)$ can be calculated. Assuming that $G(C_2H_5^+) = 0.9$ $G(C_2H_6) = 2.02 - 0.9 = 1.12$, $\Delta G(C_3H_8) = \Delta G(CH_3^\bullet) = 0.2$ which is equivalent to $\Delta G(C_2H_6) = 0.1$, and therefore a maximum value for $G(C_2H_6)$ is 1.02. From the experimental results $G(C_2H_6)$ is 1.53. If the only effect of the water

is to remove CH_5^+ and C_2H_5^+ , and that CH_5^+ does not give rise to ethane, then the results obtained indicate that $G(\text{C}_2\text{H}_5^+)$ is about 0.5.

There is a slight increase in the rate of formation of hydrogen in the presence of water (Table 15 page 151). If the H_3O^+ formed by reactions 67 and 68 decomposes on neutralisation to give $\text{H}_2\text{O} + \text{H}^\cdot$ an increase in $G(\text{H}_2)$ would be expected from methane plus water vapour compared with pure methane. Some of the hydrogen atoms would be removed by ethylene. The calculation of the change in $G(\text{H}_2)$ is also complicated by not knowing the fate of CH_5^+ in pure methane, whether it gives rise to hydrogen or any other ion or not.

If H_3O^+ is neutralised to form $\text{H}^\cdot$ and $\text{OH}^\cdot$ radicals (85), the $\text{OH}^\cdot$ radical may react with methane to form methyl radicals.



This would explain why $G(\text{C}_2\text{H}_6)$ is greater than expected, i.e. 1.53 instead of 1.02 as calculated. Recent evidence (86) indicates that neutralisation of H_3O^+ does not give rise to hydroxyl radicals. Also experiments carried out in the presence of propylene and water vapour do not indicate that hydroxyl radicals play any major part in product formation.

From these observations if water does remove CH_5^+ and C_2H_5^+ , neither of these ions can play a major part in the

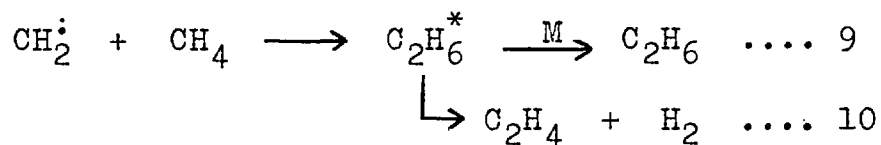
formation of the products. The product yields are not altered to the extent expected from the previous values quoted for $G(\text{CH}_5^+)$ and $G(\text{C}_2\text{H}_5^+)$. The rôle of the ethyl ion would possibly be more important than that of CH_5^+ since part of the ethylene formed can be accounted for by the increase in the propane and butane yields. Thus in pure methane radiolysis it must be questioned whether CH_5^+ does react to give ethane (via $\text{CH}_5^+ + \text{RH} \rightarrow \text{C}_2\text{H}_5^+ \xrightarrow{\text{RH}} \text{C}_2\text{H}_6$). The formation of ethane can be explained on a radical scheme plus C_2H_5^+ hydride ion transfer reactions (page 169).

Section 2.8 Methane plus Water Vapour and Oxygen.

In the radiolysis of methane plus water vapour, any ethylene that might be formed will be removed by reaction with hydrogen atoms. In order to protect the ethylene formed, oxygen was added. The G-values for the hydrocarbon products measured are given in Table 11 page 112. The hydrogen and ethane yields are the same as were obtained from methane plus oxygen. The ethylene yield is approximately twice the amount noted from methane plus oxygen. No higher hydrocarbons were found to be present.

The increase in $G(\text{C}_2\text{H}_4)$ is about 0.42 and is similar to the value obtained for $G(\text{C}_2\text{H}_5^+)$ from the product yields from the radiolysis of methane plus water vapour. The remaining ethylene formed in this system presumably

arises from reactions of the methylene radical.

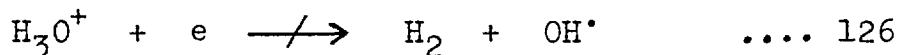


No ethyl radicals are formed from the neutralisation of C_2H_5^+ since the yields of acetaldehyde and ethanol are no greater than were obtained from methane plus oxygen radiolysis. Normal-butane was not formed at all.

The G-value obtained for ethylene formation is thought to represent a maximum value. It is less than the initial $G(\text{C}_2\text{H}_4)$ of 1.4 proposed by Hummel (20), or the value for $G(\text{C}_2\text{H}_4)$ of about 1.1 calculated by Hauser (38).

No propane, normal- or iso-butane were noted as products. In the radiolysis of methane plus oxygen, where the radicals are scavenged by oxygen, these products are formed in very small amounts. Their formation can only be via the reactions of ions. This is confirmed by the results found when water vapour is added to methane plus oxygen prior to radiolysis, as the secondary ions are removed by the water and no hydrocarbons higher than C_2 are present.

That there is no increase in the hydrogen yield (c.f. $\text{CH}_4 + \text{O}_2$) shows that the neutralisation of H_3O^+ does not give hydrogen molecules and hydroxyl radicals.

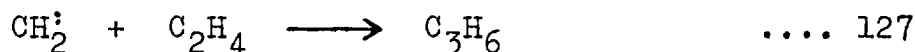


There is also no indication that any hydroxyl radicals

which may be present react with methane to give methyl radicals. The methyl hydroperoxide yield is constant, but the methanol yield decreases and this indicates a drop in $G(\text{CH}_3^\cdot)$. (Unless methanol is formed from, or in part from, CH_5^+).

Section 2.9 Methane plus Ethylene and Oxygen.

The hydrogen and ethane yields are the same as were observed from the radiolysis of methane plus oxygen, $G(\text{H}_2) = 2.85$ and $G(\text{C}_2\text{H}_6) = 0.19$. The very small amount of acetylene formed can be accounted for by the direct radiolysis of the ethylene additive. The most significant feature is the appearance of propylene with a G-value of 0.25. This product is attributed to reaction between methylene radicals and ethylene, the propylene being protected from hydrogen atom attack by the oxygen and the ethylene. No propylene was found present in the methane plus ethylene system (Table 16 page 156).



Ethane is derived from an analogous reaction of $\text{CH}_2^\cdot$ with methane, reactions 8 and 9. Thus a minimum G-value for methylene formation (since $G(\text{C}_2\text{H}_4)$ is not known in this experiment) is $G(\text{C}_2\text{H}_6) + G(\text{C}_3\text{H}_6) = 0.45$. Methylene radicals do not react appreciably with oxygen (83), but they react very rapidly with ethylene and methane.

Table 16.

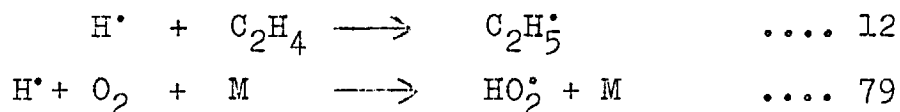
G-values for Hydrogen and the Major Hydrocarbon Products from the Radiolysis of $\text{CH}_4 + \text{C}_2\text{H}_4$, and $\text{CH}_4 + \text{C}_2\text{H}_4 + \text{O}_2$.

System.	<u>G-values</u>	
	$\text{CH}_4 + \text{C}_2\text{H}_4$	$\text{CH}_4 + \text{C}_2\text{H}_4 + \text{O}_2$
Product.		
H_2	3.0 ± 0.3	2.85 ± 0.3
C_2H_2	-	0.007
C_2H_6	1.26	0.19
C_3H_6	-	0.245
C_3H_8	1.31	0.0
iC ₄ H ₁₀	0.12	0.05
nC ₄ H ₁₀	1.18	0.003

Iso-butane is formed in amounts similar to those obtained from pure methane (Table 14 page 144), and is considered to be formed from reactions involving ions. The reaction probably involves the sec-propyl ion, which is present in pure methane with a G-value of about 0.06 (23).

The G-value for the formation of n-butane was very small but G(aldehyde) and G($\text{C}_2\text{H}_5\text{OH}$) increased compared with the values measured from the radiolysis of methane plus oxygen (Table 11 page 112). These observations are consistent with kinetic considerations for the competition of ethylene and oxygen for hydrogen atoms. At the

concentrations of ethylene and oxygen used in this experiment, some ethyl radicals are formed.



$$k_{12} = 6 \times 10^{-11} \text{ cc/molec/sec (47)}$$

$$k_{79} = 3.7 \times 10^{-32} \text{ cc}^2/\text{molec}^2/\text{sec (47)}$$

The rate of formation of ethyl to hydroperoxy radicals is 1 to 4. The presence of ethyl radicals would lead to ethyl peroxy radicals being formed, subsequent reactions leading to the formation of acetaldehyde and ethanol. Reactions of ethylene with oxygen atoms, formed by dissociative electron capture, could give rise to the same products as are thought to be derived from ethyl radicals and oxygen.

Comparing the product yields with those obtained from methane plus ethylene (Table 16 page 156), oxygen is obviously having a very marked effect on product formation. It could be considered that oxygen simply and effectively removes radicals.

Section 2.10 Methane plus Oxygen, 0.026 and 2%.

The hydrogen, ethane, propane, and ethylene yields are the same at both oxygen concentrations. This is to be expected since oxygen very efficiently scavenges hydrogen atoms and methyl radicals. The G-values are in agreement

with those obtained by Hummel at dose-rates of about 10^{14} eV/ml/min and 10^{17} eV/ml/min, at atmospheric pressure in the presence of 10% oxygen (47).

Using nitric oxide as a radical scavenger the G-value for hydrogen formation is about 3.7 (16, 24, 35), but the ethane and ethylene G-values are in accord with those obtained in this work (Table 17).

Table 17.

G-values for Hydrogen and the Major Hydrocarbon Products from the Radiolysis of CH_4 , $\text{CH}_4 + \text{O}_2$, and $\text{CH}_4 + \text{NO}$.

System.	<u>G-values</u>					
	CH_4	$\text{CH}_4 + \text{O}_2$	$\text{CH}_4 + \text{O}_2$	$\text{CH}_4 + \text{O}_2$	$\text{CH}_4 + \text{NO}$	$\text{CH}_4 + \text{NO}$
Additive%		0.026%	2%	10%		1.5%
Product.						
H_2	5.63	2.75	2.75	2.8	3.52	3.39
C_2H_4	0.12	0.43	0.46	0.44	0.7	0.4
C_2H_6	2.02	0.2	0.135	0.146	0.16	0.12
C_3H_8	0.19	0.012	0.01	0.006	0.03	-
iC_4H_{10}	0.04	n.d.	0.02	0.0	0.0	-
nC_4H_{10}	0.06	n.d.	0.005	0.0	0.0	-
Ref:	TW	TW	TW	47	35	24

n.d. = not determined. TW = This Work.

Sieck and Johnsen noted that the yields of both hydrogen and ethane were not linear with the dose received (16). This was not observed either in this work or by

Hummel (20). From the lowest conversions used (about 0.005%) all the hydrocarbon dose-yield plots were found to be linear. Sieck and Johnsen found that the rate of formation of hydrogen from methane decreased from an extrapolated G-value of 6.47 at zero conversion, to 5.74 at conversions greater than about 0.1%. The rate of formation of ethane increased from $G(C_2H_6) \div 1$ at about 0.02% conversion, to 2.2 at conversions greater than about 0.1%. These effects were considered to be due to reactions of hydrogen atoms and ethylene, but no variation of the ethylene yield with conversion was determined. Ausloos noted a similar variation of the ethane yield with conversion in the radiolysis of methane, and attributed it to the presence of oxygen as an impurity (24). Rigorous repurification of the methane eliminated this effect. If oxygen were present in trace quantities one would expect the initial rates of formation of hydrogen and ethane to be depressed. The effects noted by Sieck and Johnsen cannot therefore be due to the presence of oxygen. The hydrogen yield would initially be depressed, and would increase as the oxygen was consumed and not decrease as was observed. This was confirmed in the experiment in which the oxygen concentration was 0.026%. Fig.14 page 118 shows the variation of the rates of formation of the hydrocarbon products with conversion, and decreasing oxygen concentration. The dose-yield plot for hydrogen has not been

reproduced, but follows a similar curve to that of ethane. $G(H_2)$ tends towards 5.5 at the higher doses.

The rate of formation of propane is linear up to a dose of 5.3×10^{19} eV and then ~~de~~creases sharply, as the oxygen is completely consumed. This observation is in accord with its being formed by radical-radical reactions. The dose-yield plot for ethane does not show the same sharp increase in slope at 5.3×10^{19} eV, suggesting that the increase in the rate of formation of this product when the oxygen is used up is not due solely to methyl radical recombination reactions.

Ethane and ethylene formed in the presence of oxygen arise from reactions of methylene radicals with methane. The G-value for methylene formation on this basis is equal to $G(C_2H_6) + G(C_2H_4)$ which is approximately 0.63. As $G(C_2H_5^+) = 0.4$ it is thus difficult to say whether the ethyl ion plays any part in the formation of ethylene. Since as was noted earlier (page 135) the $C_2H_5^+$ ion can be accounted for in terms of ethyl groups appearing in the oxygenated products, and since Ausloos (25) obtained a value for $G(CH_2^{\cdot})$ of about 0.75, it would appear that $C_2H_5^+$ does not contribute to ethylene formation.

The fate of the CH_5^+ ion is not known, the oxygen concentration is far greater than that of the hydrocarbon ion scavengers (i.e. the products) and it therefore possibly reacts with the ions.

Section 2.11 Methane plus Mercury.

The results obtained are given in Table 12 page 115 . Mercury has very little effect on the product distribution, the results being within the experimental error. Trace amounts of mercury are not likely to have any effect on the formation of the products in the radiolysis of methane.

Section 2.12 Methane Irradiated at -78°C .

Compared with the G-values obtained for product formation at 20°C the hydrogen, ethane, and butane values decreased, and a slightly larger figure was obtained for ethylene. The rate of formation of ethylene increased rapidly to a maximum and then decreased with increasing dose (Fig.13 page 117).

Table 18.

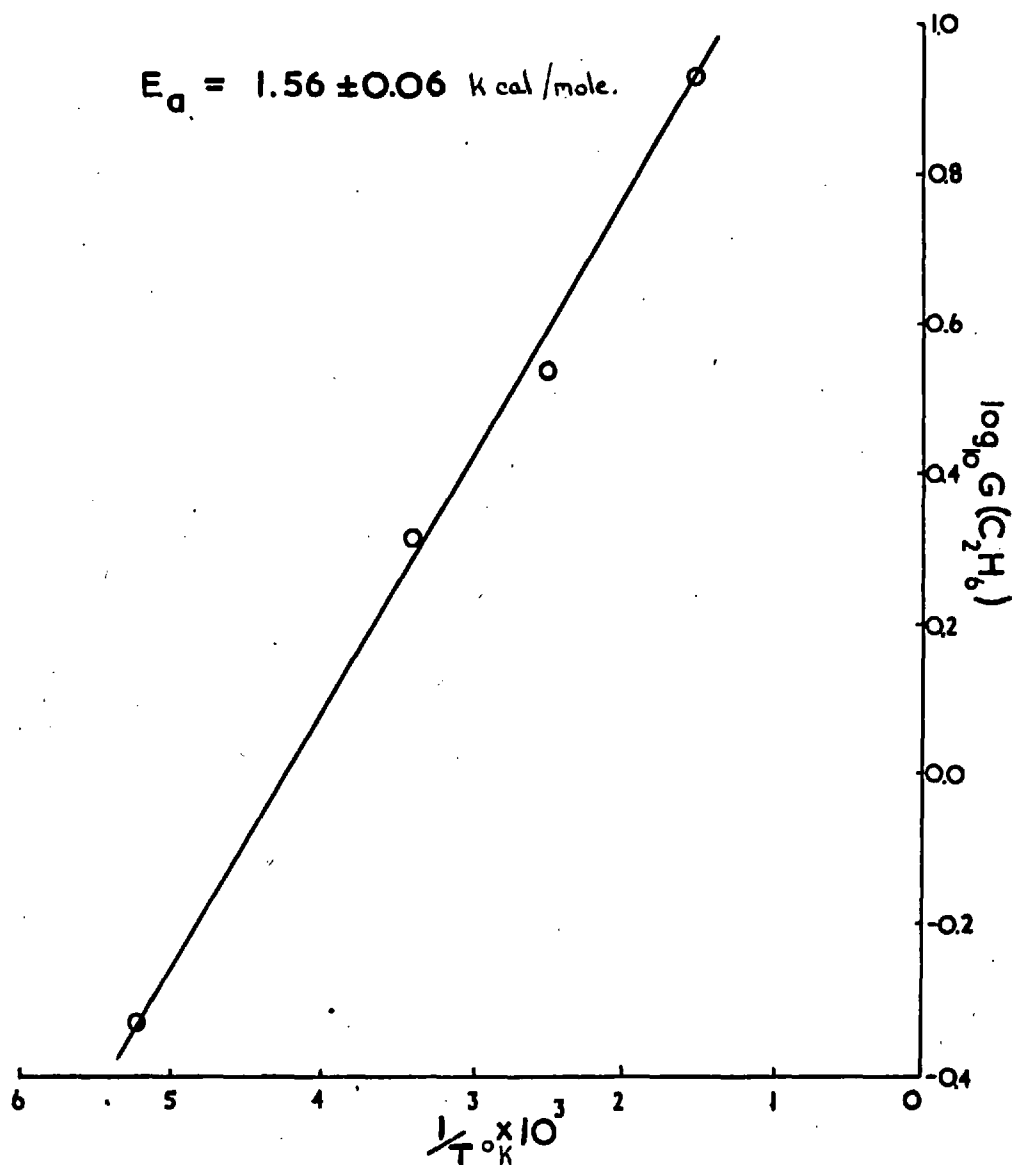
Initial G-values for the Formation of Hydrogen and the Major Hydrocarbon Products from the Radiolysis of Methane at -78°C , and 20°C .

Conditions. Products.	<u>G-values</u>		
	20°C	-78°C	-78°C (31)
H_2	5.63	3.3	4.6
C_2H_4	0.12	0.14	0.1
C_2H_6	2.02	0.46	0.7
C_3H_8	0.19	0.2	
iC_4H_{10}	0.04	0.005	
nC_4H_{10}	0.06	0.002	

The decrease in $G(H_2)$ and $G(C_2H_6)$ is in accord with results obtained by Maurin at a dose of 33.3 M rad and 400 mm Hg pressure. Since the main hydrocarbon product yields from methane irradiated at 20°C are linear with dose up to very high doses (13), the value obtained for $G(C_2H_6)$ obtained by Maurin may be taken as an approximate value for the initial formation of ethane.

An Arrhenius plot for the ethane yield has been drawn Fig.22 page 163. The G-values at the two higher temperatures are those obtained by Hummel (87). The activation energy determined from the slope of the graph is 1.56 ± 0.06 kcal/mole.

All that may be said at this moment concerning the variation of the $G(C_2H_6)$ with temperature is that ethane is formed in part by a reaction having a small activation energy. If the effect of the radiation is to produce the same species at all temperatures, then as ethane is not being formed at the lower temperature, an increase in the yield or yields of some other product(s) should occur. This does not happen to any appreciable extent (Table 18 page 161), unless the rate of formation of higher hydrocarbons (C_5 and greater) or polymer increases. The G-values for the former were not measured, and the G-value for the latter does not appear to be much greater than the other values calculated (Table 19 page 165). $G(CH_4 \text{ forming polymer})$ is 3.2. Maurin observes that in the radiolysis



Arrhenius plot for ethane from the radiolysis of methane.

Fig. 22

of methane at -78°C , the number of carbon atoms in the 'heavy' products is 5, whereas at 100°C the number of carbon atoms decreased to 3.2. The conversions used were however very high, of the order 23 to 56%.

Section 2.13 Polymer Formation.

From the G-values for the formation of the products obtained in the presence and absence of the scavengers, G-values for polymer formation have been calculated. The ratio of methyl to methylene groups in the polymer has been assumed to be 1.8 (page 46). The total hydrogen and carbon yields appearing in the products which have been measured have been determined. The amount of hydrogen that ought to be associated with the carbon present was deducted from the total hydrogen yield obtained. This excess represents the difference between the hydrogen associated with the carbon consumed to form the polymer, less that actually in the polymer. For every 1.8 methyl groups plus 1 methylene group in the polymer $1.8/2 \text{ H}_2$ and 1 H_2 molecules are liberated, since $\text{CH}_4 \longrightarrow \text{CH}_3^{\cdot} + \text{H}^{\cdot}$ and $\text{CH}_4 \longrightarrow \text{CH}_2^{\cdot} + \text{H}_2$. Thus for every three carbon atoms in the polymer 1.9 hydrogen molecules are formed. One excess hydrogen molecule therefore represents $3/1.9$ carbon atoms, and the G-value for polymer formation may be calculated in terms of carbon consumed to form the polymer. The G-value for methane consumption equals G(carbon in the products) plus G(carbon forming the polymer). The G-values

obtained are given in Table 19 below. $G(\text{polymer})$ was found to be approximately 4, and $G(-\text{CH}_4)$ about 9. A comprehensive table of the values of $G(-\text{CH}_4)$ determined by several workers was given by Maurin (31). At the lower doses $G(-\text{CH}_4)$ is of the order of 8.5 ± 1.5 .

Table 19.

G-values for Polymer Formation and for Methane Consumption in the Radiolysis of Methane at -78°C and 20°C , and Methane plus Additives at 20°C .

G-values

System.	CH_4	CH_4	$\text{CH}_4+2\%\text{O}_2$	$\text{CH}_4+\text{O}_2+\text{C}_3\text{H}_8$	Exptal	Average Value
Excess H_2	2.69	2.13	1.56	1.75		
$G(-\text{CH}_4 \text{ P})^*$	4.05	3.2	2.34	2.63	1 to 9	3.7 ± 1.3
$G(-\text{CH}_4 \text{ T})^{**}$	9.3	5.03	7.83	8.74		9 ± 1
Temperature	20°C	-78°C	20°C	20°C	20°C	

* $G(-\text{CH}_4 \text{ P}) = G(-\text{CH}_4 \text{ consumed to form the polymer})$

** $G(-\text{CH}_4 \text{ T}) = G(-\text{CH}_4 \text{ Total})$

The G-value for polymer formation is of the order expected if the number of carbon atoms per molecule is about 10 to 15, since then $G(\text{polymer})$ is approximately 0.25 to 0.4. The figure obtained experimentally only gives a very rough indication of the order of magnitude of $G(-\text{CH}_4 \text{ forming the polymer})$.

The calculated G-values for polymer formation rely

very much on the hydrogen yield. For pure methane and methane plus oxygen and propane, the values for $G(H_2)$ are in good agreement with those quoted in the literature (20, 24). From methane plus oxygen, $G(H_2)$ agrees well with that determined by Hummel (20) but is somewhat lower than the values obtained by Yang, Ausloos, and others (36, 24, 16). This may account for the rather low value for $G(-CH_4 \text{ forming polymer})$ from methane plus oxygen compared with the other values obtained.

Section 3.CONCLUSIONS.Section 3.1 Methane plus Oxygen.

The results obtained from the systems irradiated show that methyl hydroperoxide and methanol are the major oxygenated products. Methyl hydroperoxide is formed by radical reactions. Methanol probably arises from radical reactions but there is some evidence that the CH_5^+ ion may play a part in its formation.

Ethylene and ethane are the only major hydrocarbon products formed. Other workers have suggested that these products are derived from reactions of the methylene radical with methane. There is some evidence to support this mechanism, since the propylene formed in the radiolysis of methane plus oxygen and ethylene, is probably derived from reactions of the methylene with ethylene.

The hydrogen product formed is molecular hydrogen, and arises from several sources. Molecular hydrogen is obtained on the formation of $\text{CH}_2^{\cdot}$ and CH_2^+ by direct radiolysis of methane, from ion-molecule reactions between CH_3^+ , CH_2^+ , and probably other ions, and methane. The extent to which these separate reactions occur is not known. The hydrogen yield is fairly independent of the nature of the hydrogen atom scavenger used, and is not appreciably affected when the ion scavengers water and propane are added to methane plus oxygen prior to irradiation. This implies that the ion-molecule reactions giving

rise to hydrogen are very fast and are not affected by the small amounts of the additives used.

The ethylene yield is not affected by the addition of propane to methane plus oxygen, but is increased when water is used as the ion scavenger. This is thought to be due to the formation of ethylene from the reaction between the ethyl ion and water. Where the ethyl ion is not removed by water or propane it reacts with oxygen to give rise to oxygenated products containing the ethyl group. In the absence of water or propane the fate of the CH_5^+ ion is not known, but it is probable that neutralisation occurs giving methane and hydrogen atoms.

From the change in the G-value for hydrogen formation in the presence and absence of hydrogen atoms scavengers, $G(\text{H}^\bullet)$ is approximately 6. A G-value for hydrogen atom formation of about 3 must be involved in the formation of methyl hydroperoxide, together with a further $G(\text{H}^\bullet)$ of 1 for methanol formation. This leaves a $G(\text{H}^\bullet)$ of about 2 unaccounted for. From experiments where oxygen and water were present, and methane plus oxygen was irradiated at -78°C , hydrogen peroxide was found present as a product. It probably arises from reactions of the hydroperoxy radical and may be formed in the radiolysis of methane plus oxygen at 20°C . A major part of the hydrogen atoms which cannot be accounted for are probably therefore involved in hydrogen peroxide formation, the hydrogen peroxide subsequently decomposing to form water.

Section 3.2 Methane.

In the radiolysis of methane the major hydrocarbon products can be accounted for on the basis of radical reactions plus the hydride transfer reaction between the ethyl ion and the higher hydrocarbons present. The results obtained in this work do not clarify the rôle of the CH_5^+ ion in product formation.

The methyl radicals react by recombination to form ethane, and with ethyl radicals to give propane. The recombination of ethyl radicals gives rise to normal butane. The ethyl radicals are formed from the reaction between ethylene and hydrogen atoms. The G-value for the formation of methyl radicals is approximately 4, and that for methylene formation is about 0.63.

The G-value for the formation of the polymer in terms of methane consumed to form the polymer is 3.7 ± 1.3 . The G-value for the consumption of methane is approximately 9 ± 1 .

Section 4. Suggestions for Further Work.

The investigation of the effect of surface area on product formation from methane plus oxygen irradiated at -78°C and 20°C , and the experiments to determine whether hydrogen peroxide is formed at 20°C , have been proposed earlier.

Ammonia has been stated to be an efficient ion

scavenger, it would be useful to compare the effects of this scavenger with those obtained using water vapour.

Results obtained from the radiolysis of methane plus propane, and methane plus propane and oxygen, differ from those obtained by Ausloos (24) and further experiments should be carried out to clarify the rôle of the CH_5^+ and C_2H_5^+ ions in these systems.

We have been unable to explain the formation of propane in the radiolysis of methane plus propylene, and further studies using C^{14} labelled propylene would indicate the source of this product.

A preliminary experiment, at a constant dose, has been performed to determine the rate of consumption of propylene. However this determination does not appear to give a realistic initial value for $G(-\text{C}_3\text{H}_6)$. The radiolysis of systems containing small amounts of propylene would obviously be useful.

APPENDICES.

Page.

I.	Purity of the Hydrocarbon Gases as received from British Oxygen Limited, and Calor Gas Ltd.	172
II.	Retention Times for Various Compounds on Columns DE 105, S and I.	
	a. Hydrocarbons and Oxygenated Compounds on Column DE 105.	173
	b. Hydrocarbons and Permanent Gases on Column S.	174
	c. Methane, Hydrogen, Oxygen, and Nitrogen on Column I.	175
III.	Melting and Boiling Points, and Vapour Pressures for Various Compounds.	176

APPENDIX I.

Purity of the hydrocarbon gases as received
from British Oxygen Ltd., and Calor Gas Ltd.

Percentage of gas present.

Gas.	Methane	Ethane	Ethylene	Propane	i-Butane	n-Butane.
Ethane	-	98.4	-	1.5	-	0.1
Ethylene	0.038	0.028	99.79	-	0.072	0.073
Propane	-	5.5	-	92.25	2.83	0.11
i-Butane(C)				0.53	98.97	0.5
n-Butane(C)						99.6
n-Butane	-	3.2	-	36.4	25.9	34.4

(C) = Calor Gas Ltd.

APPENDIX II (a)

Retention times for some hydrocarbon and oxygenated compounds. Column D E 105, 2m polyethylene glycol on chromosorb P.

Conditions.	80°C, 60ml/min. argon flowrate	80°C, 45ml/min. argon flowrate	60°C, 50ml/min. argon flowrate
Compound.	Needle No.20	Needle No.12	Needle No.12
Acetaldehyde	2m 9s	2m 22s	3m 48s
Acetone	4m 30s	4m 26s	
Diethyl Ether	1m 25s	1m 24s	
Dioxan	16m 30s		
Ethyl Alcohol	8m 47s	9m 30s	21m 30s
Ethylene Glycol	23m		
Ethylene Oxide		2m 20s	
Formaldehyde	7m 20s	8m 20s	
Formic Acid	~ 24m		
Methyl Alcohol	7m 20s	8m 20s	16m 30s
Methyl hydroper- oxide	7m 20s	8m 10-20s	
i-Propyl Alcohol			20m 35s
Water	~ 30m		
Methane	37s		
Ethane	42s		
Ethylene	43s		
Propane	46s		
i-Butane	49s		
n-Butane	49s		

APPENDIX II (b)

Retention times for some hydrocarbon compounds
and permanent gases on Column S

2½% di-2-ethyl hexyl sebacate.

Conditions.	80°C, 60ml/min argon flowrate	35°C, 50ml/min argon flowrate	0°C, 30ml/min [*] argon flowrate
Compound.	Needle No. 20	Needle No. 12	Needle No. 12
Methane	1m 7s	1m 28s	1m 57s
Acetylene		15m 20s	
Ethylene	2m 30s	5m 25s	7m 25s
Ethane	1m 48s	3m 16s	4m 15s
Propylene		26m	
Propane	3m 12s	8m 27s	10m 16s
i-Butane	5m 31s	18m 20s	23m 5s
n-Butane	6m 18s	22m 30s	28m
i-Pentane	11m 20s		
n-Pentane	11m 34s		
2-methyl pentane	19m		
2-2 Dimethyl pentane	18m 20s		
2-3 Dimethyl pentane	20m 20s		
Hydrogen	54s	61s	
Oxygen		1m 13s	
Nitrogen		1m 13s	
Carbon Dioxide		1m 33s	

* The temperatures given above are those at which the column was set on the temperature control unit. The 80° and 35° temperatures are correct, the 0°C corresponds to 36° C in the oven.

APPENDIX II (c)

Retention times for methane, hydrogen, oxygen,
and nitrogen.

Column I, Molecular sieve.

Conditions.	2m column 35°C, 40ml/min argon flowrate
Compound.	Needle No.12
Methane	2m 30s
Hydrogen	49s
Oxygen	1m 17s
Nitrogen	1m 42s

APPENDIX III.

Melting and boiling points, and vapour pressures for various compounds from the Handbook of Chemistry and Physics 41st Edn.

Compound	M. Pt. °C	B. Pt. °C	Vapour Pressure mm Hg.	
			-196°C	-78°C
Metnane	-184	-161.5	9.7	
Ethane	-172	- 88.3		
Propane	-189.9	- 42.2	1*	
i-Butane		- 10	1*	20
n-Butane	-135	-0.6 to -0.3	1*	10
neo-Pentane		9.5	1*	10
iso-Pentane		28	1*	2
n-Pentane	-131	36	1*	1
Ethylene	-169.4	-103.9	1*	
Propylene	-185	- 47	1*	
Acetylene	- 81.8	- 83.8	s	
Hydrogen		-253		
Oxygen	-218	-183		
Nitrogen	-210	-195.8		
Carbon				
Dioxide	- 57.5		s	
Methanol	- 97.8	64.7		1*
Ethanol	-117.3	78.5		1*
Formaldehyde	- 92	- 21	s	20
Acetaldehyde	-123.5	21	s	2
Ethylene				
oxide	-111.3	10.7		
Dimethyl				
ether	-138.5	- 23.7	1*	40
Acetone	- 95	56.5		1*

1* denotes that the vapour pressure is less than 1 mm Hg.

s = solid.

REFERENCES.

- No.
1. P. Harteck and S. Dondes
Nucleonics 14 1956 7 22.
 2. C. G. Edwards and F. Mosley
A.E.R.E. C/R 2710 1958
 3. A. K. Wieber, G. W. Kinzer and W. P. Conner
Nucleonics 19 1961 2 50
 4. M. R. Galley. Fission Fragment Irradiation
of Methane. Ph.D Thesis
Univ. Lond. 1964
 5. R. L. Platzman.
J. Phys. Radium 21 1960 853
 6. S. C. Lind and D. C. Bardwell
J. Am. Chem. Soc. 48 1926 1575
 7. G. G. Meisels, W. H. Hamil and R. R. Williams
J. Chem. Phys. 25 1956 790
 8. G. G. Meisels, W. H. Hamil and R. R. Williams
J. Phys. Chem. 61 1957 1456
 9. R. R. Williams and L. H. Gevantman.
J. Phys. Chem. 56 1952 569
 10. D. P. Stephenson and D. O. Schissler.
J. Chem. Phys. 23 1955 1353
 11. D. P. Stephenson and D. O. Schissler.
J. Chem. Phys. 24 1956 926
 12. F. H. Field, J. L. Franklin and F. W. Lampe.
J. Am. Chem. Soc. 78 1956 5697
 13. F. W. Lampe and F. H. Field.
J. Am. Chem. Soc. 79 1957 4244

- No.
14. S. Wexler and N. Jesse.
J. Am. Chem. Soc. 84 1962 3425
15. F. H. Field and M. S. B. Munson
J. Am. Chem. Soc. 87 1965 3289
16. L. W. Sieck and R. H. Johnsen
J. Phys. Chem. 67 1963 2281
17. F. P. Abramson and J. H. Futrell
J. Chem. Phys. 45 1966 1925
18. F. W. Lampe
J. Am. Chem. Soc. 79 1957 1055
19. M. S. B. Munson and F. H. Field
J. Am. Chem. Soc. 87 1965 3294
20. R. W. Hummel
Disc. Far. Soc. 36 1963 75
21. V. Aquilanti
J. Phys. Chem. 69 1965 3434
22. F. Cacace, G. Ciranni and A. Guarino
J. Am. Chem. Soc. 88 1966 2903
23. P. J. Ausloos and S. G. Lias
J. Chem. Phys. 38 1963 2207
24. P. J. Ausloos, S. G. Lias and R. Gorden Jr.
J. Chem. Phys. 39 1963 3341
25. P. J. Ausloos, R. Gorden Jr. and S. G. Lias
J. Chem. Phys. 40 1964 1854
26. M. S. B. Munson and F. H. Field
J. Am. Chem. Soc. 87 1965 4242
27. M. S. B. Munson, F. H. Field and J. L. Franklin
J. Chem. Phys. 42 1965 442
28. D. C. Walker and R. A. Back
J. Chem. Phys. 38 1963 1526

- No.
29. R. W. Hummel
Trans. Far. Soc. No. 517 62 1966 59
30. C. E. Melton and P. S. Rudolf
J. Chem. Phys. 31 1959 1485
31. J. Maurin
J. Chem. Physique. 59 1962 15
32. D. R. Davis
Ph.D. Thesis Los Angeles Univ.
Calif. 1966
33. R. E. Honig and G. W. Sheppard
J. Phys. Chem. 50 1946 119
34. R. E. Honig and G. W. Sheppard
J. Phys. Chem. 50 1946 144
35. Kang Yang
J. Phys. Chem. 65 1961 42
36. K. Yang and P. J. Manno
J. Am. Chem. Soc. 81 1959 3507
37. B. H. Mathan and R. Mandal
J. Chem. Phys. 27 1962 207
38. W. P. Hauser
J. Phys. Chem. 68 1964 1576
39. R. H. Johnsen
J. Phys. Chem. 69 1965 3218
40. E. W. R. Steacie
Atomic and Free Radical Reactions
2nd. Edn. New York Reinhold 1954
41. L. I. Bone and R. F. Firestone
J. Phys. Chem. 69 1965 3652
42. P. Curie and M. Curie
Compt. Rend. 129 1899 823

No.

43. A. Kailan
S. B. Akad. Wiss. Wien 128 11a,
1917 8713
44. B. M. Mikhailov, M. E. Kuimova and V. S.
Bogdanov
All Union Conference on Radn. Chem.
Moscow 1957
45. G. R. A. Johnson and G. A. Salmon
J. Phys. Chem. 65 1961 177
46. J. A. Hearne and R. W. Hummel
A.E.R.E. R-4581 Feb. 1964
47. J. A. Hearne and R. W. Hummel
A.E.R.E. R-4871 Nov. 1964
48. Jer Ru Maa
Fission Fragment Induced Oxidation
of Light Hydrocarbons. Ph. D. Thesis
Pennsylvania State Univ. 1964
49. J. A. Gray
J. Chem. Soc. 3150 1952
50. J. F. Riley and T. C. Hung
Oak Ridge Nat. Lab. Report 196
51. Oxidation and Combustion Reviews Vol.1
Ed. C. F. H. Tipper Elsevier 1965
52. G. R. Hoey and K. O. Kutsche
Can. J. Chem. 33 1955 496
53. G. S. Pearson
J. Phys. Chem. 67 1963 1686
54. D. E. Hoare and A. D. Walsh
Trans. Far. Soc. 53 1957 1102

- No.
55. J. Heicklen and H. S. Johnston
J. Am. Chem. Soc. 84 1962 4030
56. E. D. Thomas, G. R. McMillan and J. G. Calvert
Quoted in Ref. 51 page 104
57. M. Barber, J. Farren and J. W. Linnett
Proc. Roy. Soc. Ser A 274 1963 306
58. D. F. Dever and J. G. Calvert
J. Am. Chem. Soc. 84 1962 1362
59. J. Farren, J. R. Gilbert, J. W. Linnett and
I. A. Read
Trans. Far. Soc. No. 496 60 1964
60. J. Heicklen
J. Chem. Phys. 42 1965 1853
61. N. R. Subbaratnam and J. G. Calvert
J. Am. Chem. Soc. 84 1962 1113
62. P. L. Hanst and J. G. Calvert
J. Phys. Chem. 63 1959 71
63. S. N. Foner and R. L. Hudson
J. Chem. Phys. 21 1953 1608
64. S. N. Finer and R. L. Hudson
J. Chem. Phys. 36 1962 2676,
2681
65. M. Shannin and K. O. Kutsche
J. Phys. Chem. 65 1961 189
66. T. H. Pratt and P. Wolfgang
J. Am. Chem. Soc. 83 1961 10
67. R. A. Back, T. W. Woodward and K. A.
McJauchlan
Can. J. Chem. 40 1962 1380

- No.
68. P. Harteck and S. Dondes
Nucleonics 14 1956 66
69. B. P. Burt and J. F. Kircher
Radn. Res. 9 1958 1
70. J. A. Hearne and R. W. Hummel
Radn. Res. 15 1961 254
71. G. R. A. Johnson
J. Inorg. Nucl. Chem. 24 1962 461
72. C. J. Hochanadel, Ghormley, and Davis
J. Phys. Chem. 56 1952 597
73. H. R. Williams and H. S. Mosher
J. Am. Chem. Soc. 76 1954 2984
74. G. R. A. Johnson and G. Scholes
Analyst 79 1954 217
75. C. N. Satterfield, R. E. Wilson and R. M. Leclair
Anal. Chem. 26 1954 1792
76. G. M. Eisenberg
Ind. Eng. Chem. Anal. 15 1943 327
77. R. D. Cadle and H. Hulf
J. Phys. Coll. Chem. 54 1950 1191
78. J. H. Knox and R. G. Norrish
Proc. Roy. Soc. 221A 1954 155
79. M. S. Matheson
Radn. Chem. Ann. Rev. Phys. Chem.
Col. 13 1962
80. J. E. Manton and A. W. Tickner
Can. J. Chem. 38 1960 858
81. A. B. Collear and W. P. D. Pereira
Trans. Far. Soc. 59 1963 2774

No.

82. B. H. Hamling et al.
Aerojet-General Nucleonics Semi-
annual Progress Report AGN 8132
July-Dec. 1964.
83. The Chemistry of Carbenes A. Ledwith
Roy. Inst. of Chem. Lecture Series
1964 No. 5
84. J. H. Futrell
Conf. on Radn. Chem. & Photochem.
Univ. Newcastle 1966
85. A. R. Anderson, B. Knight and J. A. Winter
Trans. Far. Soc. No. 518 Vol.62
1966
86. G.R.A. Johnson and M. Simic
Nature 210 1966 1356
87. R. W. Hummel
A.E.R.E. Report No. R-4838.