MERCURY PHOTOSENSITIZED OXIDATIONS IN THE GAS PHASE

BY

SHAH MOHAMMAD MANZOOR-UR-RAHMAN

A Thesis submitted for the degree of
Doctor of Philosophy in the Department
of Chemistry, University of Aston in
Birmingham.

1977

(awarded April, 1978)

TO

MY GRANDFATHER AND THE SHAHEEDS OF PAK
FORCES WHO SACRIFICED THEIR PRESENT FOR OUR
FUTURE

"MERCURY-PHOTOSENSITIZED OXIDATIONS IN THE GAS PHASE"

BY

SHAH MOHAMMAD MANZOOR-UR-RAHMAN

A Thesis submitted for the degree of
Doctor of Philosophy in the Department
of Chemistry, University of Aston in Birmingham.

1977

SUMMARY

This thesis describes experiments on the mercury-photosensitized oxidations of some hydrocarbon alkenes with molecular oxygen. Products have been identified and variations in product yields studied in detail as a function of alkene/oxygen ratio, total pressure, incident light intensity and time for 2-methyl propene. The reactions of propene and butene-1 have also been studied but in rather less detail.

To assist the interpretation of the results the reactions of the alkenes were also studied with (a) ground state oxygen atoms generated by mercury-sensitized decomposition of nitrous oxide, and (b) electronically excited oxygen molecules ($^1O_2^*$) formed in a microwave discharge through oxygen at low pressures. Comparison of the results showed that the presence of neither singlet oxygen molecules nor oxygen atoms alone was sufficient to account for the observed products of the mercury-sensitized oxidations. In fact it was necessary to include ozone as a reaction intermediate forming some of the observed products.

Plausible routes for the formation of the main reaction products and some minor reaction products have been suggested, and shown to be reasonably consistent with the observed variations in product yields with the reaction parameters. Because of the complexity of the reaction system, it was not possible to attempt to account quantitatively for the observed yields of the products.

KEY WORDS:

MERCURY
PHOTOSENSITIZED OXIDATIONS
GAS-PHASE
ALKENES

This work was carried out between 1972 and
1976 at The University of Aston in Birmingham.
It has been done independently and has not
been submitted for any other degree.

M. R. Shah

SHAH. M.M.R.

ACKNOWLEDGEMENTS

First of all, I wish to express my sincere thanks and utmost gratitude to my supervisor Dr. Stephen J. Moss for his supervision, constant encouragement and unfailing interest throughout the course of this study.

I would then thank the technical staff of the Chemistry Department for their assistance.

I would very much like to thank Mrs. Edmonds and Mrs. Weedon for their co-operation and interest in the typing of this thesis.

My thanks also go to my mother, sisters, brother, my friends Asghar and Mr. H. Raza Rizvi and his family for their help and their encouragement.

Finally I would like to thank my brother-in-laws, Mr. M.U. Khan, and my sister Farzana for their help and co-operation during all this period of study.

CONTENTS

Page

CHAPTER 1 - INTRODUCTION AND LITERATURE SURVEY

CHAPTER 2 - EXPERIMENTAL

CHAPTER 3 - RESULTS OF MERCURY PHOTOSENSITIZED OXIDATION WITH 2-METHYL PROPENE

CHAPTER 4 - RESULTS FOR MERCURY PHOTOSENSITIZED OXIDATION WITH PROPENE AND BUTENE-1

CHAPTER 5 - RESULTS OF THE REACTION OF SINGLET MOLECULAR OXYGEN (FROM MICROWAVE DISCHARGE) WITH ALKENES

CHAPTER ONE

INTRODUCTION AND LITERATURE SURVEY

1.1 PHOTOSENSITIZED REACTIONS:-

This thesis is concerned with mercury photosensitized reactions involving molecular oxygen and alkenes. The first chapter will therefore outline briefly the background relevant to photosensitized **reactions** in general, before discussing reactions of excited oxygen molecules and of oxygen atoms.

1.1.(a) Chronology of a photochemical reaction.

A photochemical reaction can be considered in three stages:

(i) Light Absorption:- During this stage, an electronically excited state is produced.

(ii) Primary photochemical processes:- These involve electronically excited states.

(iii) Secondary Reactions:- In this the various chemical species which are produced in the primary processes, their reactions are considered.

A photochemical reaction is a complex set of competing processes and to understand it one has to consider each of the above stages in some detail.

A molecule which has absorbed a quantum of radiation becomes "energy rich" or excited in the absorption process. It is well known that absorption in the wavelength region of photochemical interest leads to electronic excitation of the absorber. Absorption at longer wavelengths usually leads to the excitation of vibrations or rotations of a molecule in its ground electronic state. The energy associated with the electronic excitation is high compared with vibrational and rotational excitation. "Franck Condon principle" states that since electronic transitions are very rapid (10^{-15} sec.) compared with nuclear movements, the former will occur without changes in the internuclear distances.

The probability of occurence of an electronic transition and hence the intensity of the associated absorption band is dependant upon various factors. These factors are included in "selection rules" which govern whether a transition will be allowed (high probability) or forbidden (very low probability). Some forbidden transitions are too weak to be observed easily but dealing with polyatomic molecules the selection rules often break down to give reasonably strong absorption processes to occur.

1.1.(b) Quantum yield:-

A fundamental quantity in photochemical reactions is the quantum yield ϕ defined by

$$\phi = \frac{\text{number of molecules undergoing a particular process}}{\text{number of light quanta absorbed}}$$

A quantum yield can be defined for several processes occuring during a photochemical reaction such as primary quantum yields, product quantum yields, quantum yields of fluorescence, decomposition, rearrangement, etc. Primary quantum yields are of great theoretical importance but are difficult to estimate. Usually one measures the overall quantum yields of products. The magnitude of the quantum yield of a product (ϕ zero to 10^6) always provides information concerning the mechanism. Small quantum yields of all decomposition products ($\phi \ll 1$) indicate important deactivation, fluorescence or other processes that lead to no net chemical change. Large product quantum yields ($\phi \gg 1$) indicate the importance of a chain reaction forming these products. The variation of quantum yield with changes in the reaction variables usually provides valuable information on the reaction mechanism.

1.1.(c) Excited states:-

A molecule is said to be in an excited state after the absorption of a photon and promotion of an electron to a higher vacant orbital. These highly energetic molecules are short-lived and can often lose their excess energy and return to the stable ground state before a reaction can occur. The three types of process whereby the energy of electronically excited molecules can be dissipated are

(i) Radiative transitions,

(ii) Radiationless transitions that do not produce permanent chemical changes, and

(iii) Chemical reaction.

The radiation emitted during a radiative transition is termed fluorescence when the transition is between states of the same multiplicity and phosphorescence when it is between states of different multiplicities, i.e. for organic molecules the emitted radiation is fluorescence for the $S \longrightarrow S_0 + h\nu'$ transition and phosphorescence for the $T_1 \longrightarrow S_0 + h\nu''$ transition.

Non radiative transitions between the states of like multiplicity are termed as internal conversion. The process

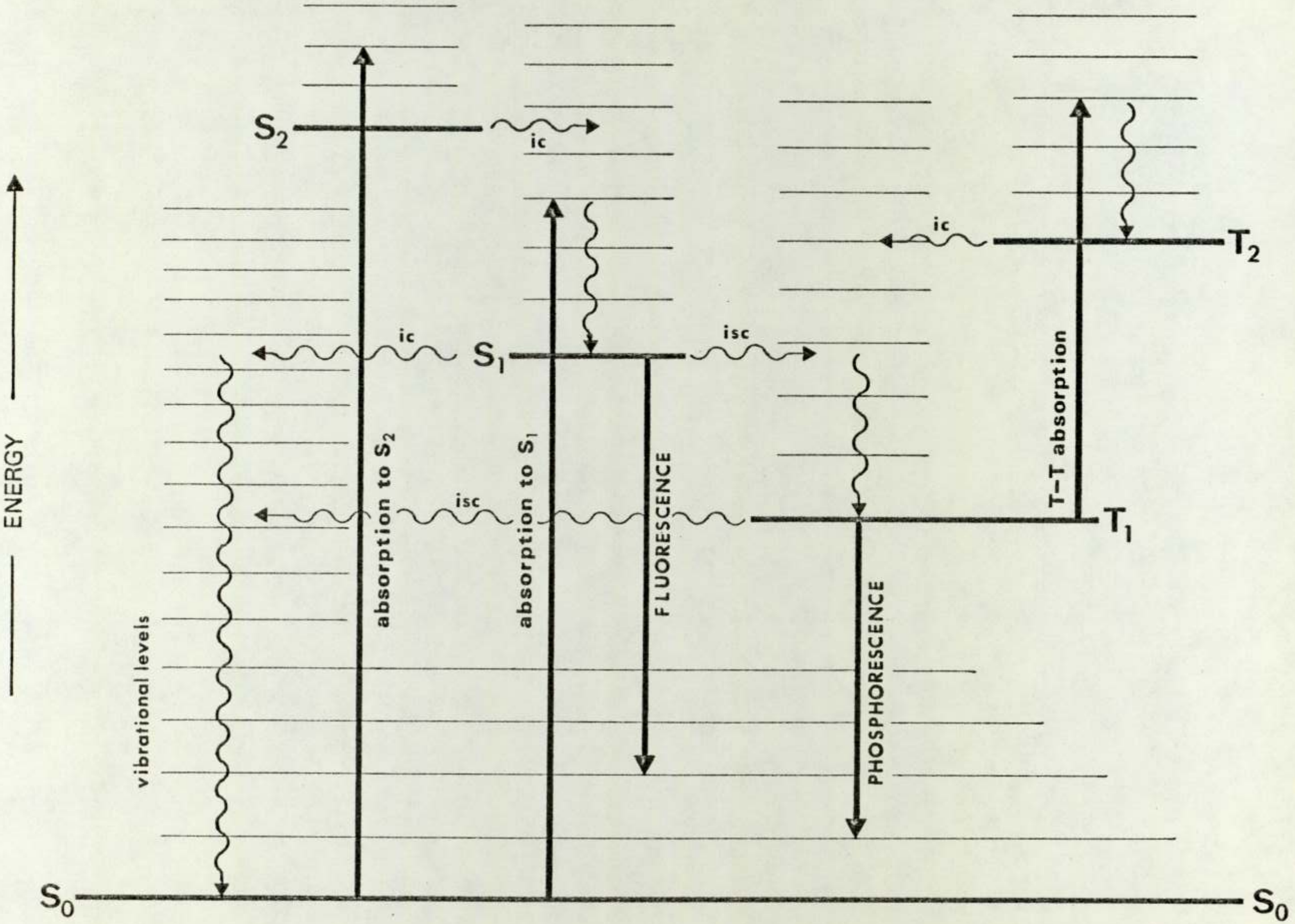

ENERGY
vibrational levels
S_2
ic
S_1
ic
isc
isc
ic
T_2
T_1
absorption to S_2
absorption to S_1
FLUORESCENCE
PHOSPHORESCENCE
T–T absorption
S_0
S_0

Figure 1.1.(c).1

is conceived of as involving iso-energetic transitions from a higher electronic state to an upper vibrational level of a lower state. The term intersystem crossing deals with the non radiative transitions between states of different multiplicity, e.g. $T_1 \rightsquigarrow S_1$. (Fig. 1.1.(c).1).

When a molecule originally excited by absorption of radiation is deactivated by interaction with other species of the system, the general term applied is "quenching". However, in some cases the disappearance of excitation in one species coincides with the appearance of excitation in some other species in the system. Such quenching steps are more appropriately labelled as "energy transfer", implying intermolecular electronic energy transfer.

In energy transfer systems, life times also play an important role. The mechanistic lifetime of a donor state is the reciprocal of the sum of the first order and pseudo-first order rate constants for all steps which depopulate that excited state of which the latter will depend on the concentration of the acceptor.

Franck$^{(1)}$ predicted early in 1922 that electronic excitation could be exchanged between atoms, and one of the earliest examples of photosensitization was the production of hydrogen atom by the effect of excited mercury atom on molecular hydrogen.

$$\text{Hg } 6\ (^3P_1) + H_2 \longrightarrow \text{Hg } 6\ (^1So) + 2H$$

This reaction was discovered by Cairo and Franck$^{(2)}$ in 1922. It is a very convenient source of atomic hydrogen since hydrogen gas does not absorb radiation in a region being under consideration.

The process of "photosensitization" involves absorption of light energy by a strongly absorbing substance, the "photosensitizer", and then the transfer of this energy by collision to another substance (the acceptor), which then undergoes chemical reactions to give products.

The obvious advantage of photosensitization is that sufficient amounts of light energy to induce chemical changes may be indirectly transferred to a substance in a convenient spectral region where it itself does not absorb. Photosensitization therefore provides valuable experimental technique which has been used with great advantage. Chemical changes which occur in the quenching molecules during or after the transfer of excitation energy and the relation of these changes to the type of photosensitizer used and the amount of energy transferred are all of interest to a chemist.

1.1.(d) Mechanism of a sensitized reaction:-

The following mechanism(3) in which S is the sensitizer, A the acceptor and superscripts indicate the multiplicities of the excited states, describe the general photosensitized reaction.

$S \xrightarrow{h\nu} {}^1S^*$	Excitation	1
${}^1S^* \longrightarrow S + h\nu'$	Fluorescence	2
${}^1S^* \longrightarrow S$	Radiationless decay	3
${}^1S^* \longrightarrow {}^3S^*$	Intersystem crossing	4
${}^3S^* \longrightarrow S$	Radiationless decay	5
${}^3S^* \longrightarrow S + h\nu''$	Phosphorescence	6
${}^3S^* + A \longrightarrow S + {}^3A$	Energy transfer	7
${}^3A \longrightarrow \text{Products}$	Reaction	8

In the ideal case, the only function of the sensitizer is to absorb light, undergo intersystem crossing to its lowest triplet state and transfer the energy to the acceptor, i.e. only reactions 1, 4, 7 and 8 are significant in photosensitized reactions. Inherent in this scheme are two important assumptions.

(i) The only interaction of sensitizer and substrate is energy transfer, and

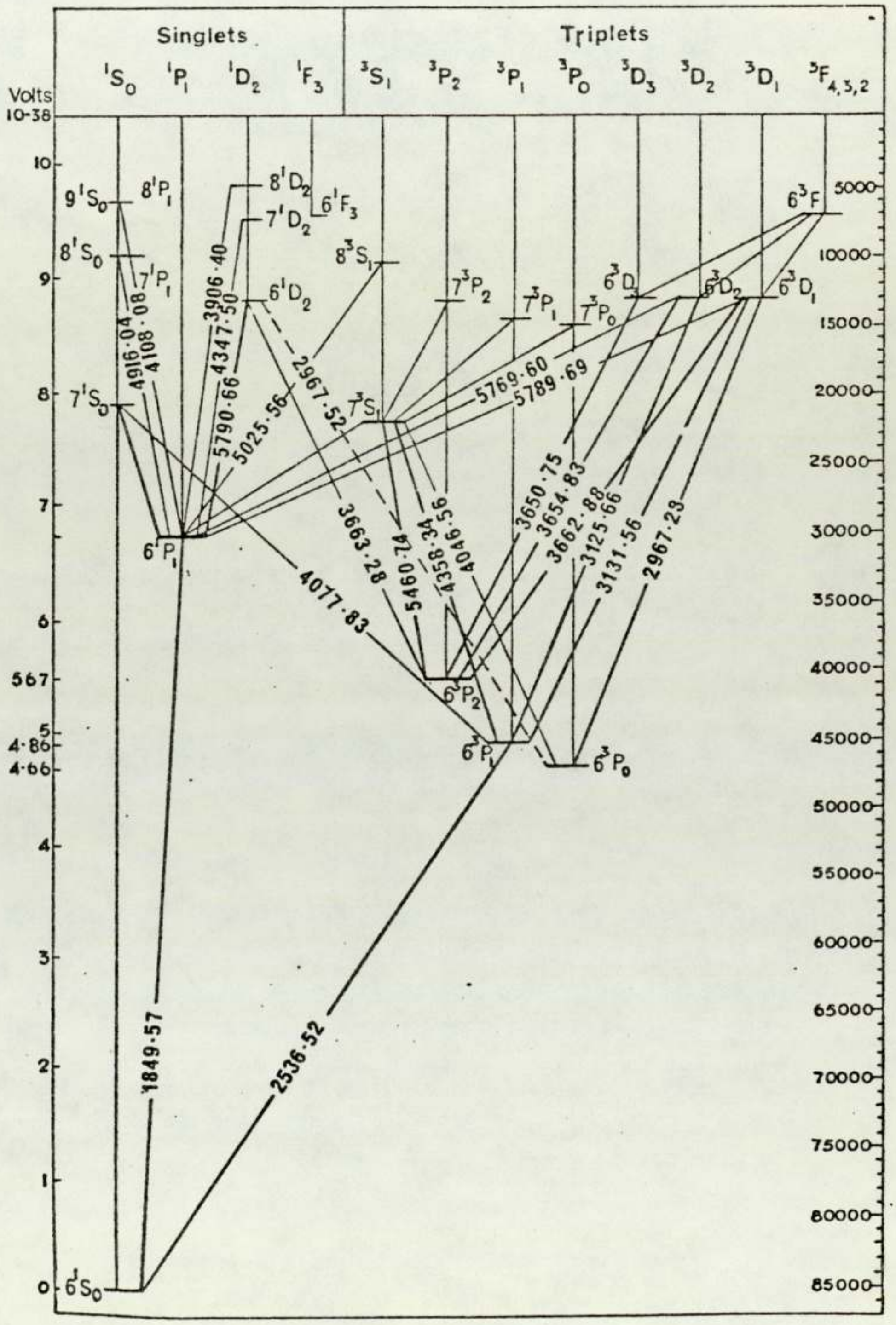
(ii) Energy is transferred from the lowest triplet state, although sometimes these assumptions unfortunately break down.

Vapours of some metals have been particularly useful as photosensitizers in the ultraviolet spectral region. The properties which a suitable metal vapour sensitizer must possess are discussed by Steacie(4) and leave the choice to mercury, cadmium and zinc. With mercury, cadmium and zinc as photosensitizers, the general behaviour of hydrocarbon and the values of their quenching cross sections appear to be, in general, consistent with the postulate that spin conservation rule is valid. (The experimental observations have been summarized by Steacie(4)). According to this rule, overall spin angular momentum must be unchanged in electronic energy transfer. In the case of triplet - singlet interaction, as in the Hg 6 ($^3P_1$) - alkene system, the rule requires

$$\text{Triplet } (S = 1) + \text{Singlet } (S = 0) \longrightarrow \text{Singlet } (S = 0) + \text{Triplet } (S = 1)$$

$$^3A^* + {}^1B \longrightarrow {}^1A + {}^3B^*$$

with alkenes and triplet metal atoms, formation of excited molecules in the primary quenching act predominates. In this case, the quenching cross sections are always large.



ENERGY LEVELS OF MERCURY

FIG. 1·2·1

1.2 MERCURY PHOTOSENSITIZED REACTIONS:-

Mercury vapour is very convenient for the studies in atomic photochemistry and an extensive literature on the behaviour of excited mercury has accumulated over the last half century. It is the most widely used gas phase sensitizer having quite significant vapour pressure at room temperature. It is also not very reactive and does not usually react chemically with other substances in the system. Recent reviews of mercury photosensitized reactions include those of Cvetanovic(5) and Gunning and Strausz(6). Important earlier references include the comprehensive review of Steacie(4) and Laidler's(7a, b, c) papers dealing with the theoretical aspects. Physical quenching processes are discussed by Pringsheim(8) and Mitchell and Zemansky(9). Excellent general treatments include those of Bowen(10), Noyes and Leighton(11) and Rollefson and Burton(12).

The excited mercury atom Hg 6 ($^3P_1$) is produced by the absorption of the 253.7 nm. mercury resonance line from a low-pressure mercury lamp (Fig. 1.2.1). In a system at very low pressures, practically all the 6 ($^3P_1$) states disappear by emission of radiation as resonance phosphorescence(13). An excited state emits resonance radiation when the emitted light has the same frequency as that obsorbed in the excitation. For the process

$$\text{Hg } 6\ (^3P_1) \longrightarrow \text{Hg } 6\ (^1So) + h\nu_p$$

the life time for this transition is 1.1 × 10^{-7} sec. and the process occurs with such high probability only because mercury is a heavy atom with appreciable (jj) coupling. The fully allowed transition ($\Delta S = 0$)

$$\mathrm{Hg}\ 6\ (^1P_1) \longrightarrow \mathrm{Hg}\ 6\ (^1S_0) + h\nu_f\ (184.9\ \mathrm{nm.})$$

has a lifetime of 1.3×10^{-9} sec. The absorption of the 184.9 nm. resonance radiation by mercury is extremely high. The relatively long lifetime of the Hg 6 ($^3P_1$) state reflects the forbidden nature of the triplet ⟶ singlet intersystem crossing.

The processes

$$\mathrm{Hg}\ 6\ (^1S_0) + h\nu \longrightarrow \mathrm{Hg}\ 6\ (^3P_0)$$

and its reverse do not occur because

$$J = 0 \not\leftrightarrow J = 0 \text{ and } \quad \Delta S = 0$$

The Hg 6 ($^3P_0$) state is an example of a metastable state. It cannot readily relax by emission ($T \approx 10^{-3}$sec.) to the ground state for reasons which give rise to the selection rules ($J = 0 \not\leftrightarrow J = 0$).

Of the above mentioned two, the radiation of 184.9 nm. is absorbed strongly by oxygen and ordinary quartz. For absorption of 253.7 nm. radiation by mercury in the reaction cell to be effective, it is important that the line shapes of absorbing and emitting system should match as closely as possible. In the high pressure u.v. lamps, the line shape is considerably broadened by collisions. (Collision broadening). In addition to this, although the total output is very high, the emission is largely above 300.0 nm. The 253.7 nm. line is almost entirely lost by self absorption in the lamp. This phenomenon of self absorption is minimised by using a mercury resonance lamp (or low pressure lamp), which has strong emission of the unreversed resonance lines at 253.7 nm. These usually contain a small amount of metal vapour, e.g. mercury, cadmium, zinc, etc., and several millimeter pressure of a rare gas. They operate at relatively low current and high voltages.

If in a system containing excited mercury in the 6 ($^3P_1$) state a foreign gas is added, the energy transfer to the gas molecules (Quenching) can take place via three main types, i.e. three types of quenching have been differentiated$^{(5)}$.

i) $Hg\ ^3P_1 + A \longrightarrow Hg\ ^3P_o + A$ (20.9 K J.)

ii) $Hg\ ^3P_1 + A \longrightarrow Hg\ ^1S_o + A^*$ (469.7 K J.)

iii) $Hg\ ^3P_1 + A \longrightarrow Hg\ ^1S_o + A_1 + A_2$ or $Hg\ A_1 + A_2$

where A is the quenching molecule.

In process (i), the quenching of triplet state mercury to metastable 6 ^3P_o state occurs. Transitions from this state to the ground state are strongly forbidden and hence species in this state are relatively long lived (10^{-3} sec.). This type of quenching takes place with the transfer of only 20.9 K J.mol^{-1} energy to the quenching molecule.

In process (ii), the direct quenching of Hg 6 $^3P_1$ to the ground state occurs with a transfer of 468 K J.mol^{-1} of energy to the quenching molecule, which raises the electronic level to an excited state, e.g. Alkenes have their lowest singlets well above the $^3P_1$ state, but their first triplets lie below, so process (ii) triplet transfer is feasible energetically and obeys the Wigner rule. The experimental results to date support such an excited molecule mechanism.

Process (iii) involves the transfer of energy again, but in this case the quenching molecule breaks up, i.e. it fragments. Quenching by alkanes is usually of this type where the energy is quite sufficient to break the C - H bond.

In the light of the important findings of Callear and Norrish$^{(14)}$ who made the observation that, although metastable

6 ^3P_o atoms are formed when quenching the $^3P_1$ state by N_2, H_2O and CO, these atoms were not produced in quenching by H_2, C_2H_4, C_2H_6, O_2, NO and N_2O, hence the possible chemical reactions initiated by ^3P_o mercury atoms will not be considered.

Cvetanovic(15) has reviewed the detailed studies of mercury photosensitized reactions up to 1962 and dealt further with the reactions of alkenes with oxygen atoms produced by the mercury photosensitized decomposition of nitrous oxide (53-56). The technique has been successfully applied as a good source for the production and reactions of oxygen atoms in the gas phase. Before proceeding to the oxygen atom reactions, some typical primary processes in mercury photosensitization are discussed below.

1.2(a). Decomposition of Hydrogen, Hydrogen chloride, Methyl chloride and Di methyl Ether:-

Detailed studies[2, 14, 6, 16 - 23)] have shown the following primary processes for the reactions of above compounds with Hg 6 $^3P_1$ atom:

(i) $Hg\,(^3P_1) + H_2 \longrightarrow Hg\,H + H$

(ii) $Hg\,(^3P_1) + HCl \longrightarrow HgCl + H$

(iii) $Hg\,(^3P_1) + CH_3Cl \longrightarrow HgCl + CH_3$

(iv) $Hg\,(^3P_1) + CH_3COCH_3 \longrightarrow Hg\,(^1S_o) + CH_3COCH_2 + H$

1.2.(b) Alkanes:-

The major products of the Hg ($^3P_1$) sensitized reactions of alkanes, RH at room temperature are typical of those expected from secondary reactions of alkyl radicals and hydrogen atoms, that is, hydrogen, the radical recombination products R_2, and olefins formed from disproportionation reactions of the alkyl radicals. In each case the products are consistent with the primary quenching act being a C - H bond scission. Mercury hydride HgH, has been suggested as an unstable intermediate in the quenching of alkanes and this seems reasonable. However, there is no direct evidence for its formation.(24)

Low primary quantum yields were first reported for Hg 6 $^3P_1$ sensitized reactions with the alkanes. Subsequently, it was realized that hydrogen atoms formed in the primary act add rapidly to the alkenes formed in the secondary disproportionation reactions and that the low quantum yields were due to this self-scavenging.(25 - 29)

1.2.(b).1. Decomposition of n-Butane:-

This reaction has been studied in detail by Cvetanovic, Falconer and Jennings(28) who showed that the experimental behaviour of the system could be explained without having to invoke the occurence of metastable mercury atoms. It has been reported by Callear and Hedges(19) that HgH is not produced in the reaction of Hg 6^3P_1 with saturated hydrocarbons. They suggest that the primary process is either

$$\mathrm{Hg\ 6\ (^3P_1) + RH \longrightarrow Hg + R. + H.}$$

or

$$\mathrm{Hg\ 6\ ^3P_1 + RH \longrightarrow HgR + H.}$$

This reaction is much used as a source of hydrogen atoms for quantitative studies.

1.2.(c) Alkenes:-

In sharp contrast to alkanes, the quenching cross sections of alkenes are large (e.g. $\sigma^2Q = 4.6$ & $0.23\ \mathrm{nm}^2$ for propene and propane respectively) and the rates of their reactions decrease as the pressure is raised. Quenching by energy transfer predominates, although there are indications that a primary C - H bond split occurs as well. LeRoy and Steacie(30) proposed for ethylene that triplet energy transfer produced a relatively short lived (10^{-9} sec.) vibrationally excited triplet,

$$\text{Hg } 6\ (^3P_1) + C_2H_4 \longrightarrow {}^3C_2H_4 + \text{Hg } 6\ ^1S_0$$

which could decompose, because of this excess vibrational energy. The major products of the reaction are hydrogen and acetylene. Their quantum yields are about 0.4 each(31) and are temperature independant; these values decrease as the pressure of C_2H_4 is increased or inert gas CO_2 is added.(32)

These facts suggest an excited molecule mechanism and excellent evidence for this was obtained by Cvetanovic and Callear.(32) They further assumed that two electronically and vibrationally excited states of approximately equal lifetimes were involved in the overall reaction(33); both were subject to collisional deactivation but only one decomposed.

$$C_2H_4 + \text{Hg } 6\ (^3P_1) \longrightarrow C_2H_4^* + \text{Hg } 6\ ^1S_0$$

$$C_2H_4^* \longrightarrow C_2H_4^{**}$$

$$C_2H_4^* + C_2H_4 \longrightarrow 2\ C_2H_4$$

$$C_2H_4^{**} \longrightarrow C_2H_2 + H_2$$

$$C_2H_4^{**} + C_2H_4 \longrightarrow 2\ C_2H_4$$

Rabinowitch et al(34) investigated the Hg 6 $^3P_1$ reaction with transethylene -d_2 and found as major products Cis $C_2H_2D_2$ unsym-$H_2C{:}CD_2$ and isotopically mixed acetylenes and hydrogens. Their proposed mechanism involves two excited states and is basically that of Callear and Cvetanovic.(32)

Dissociation of C-C bond becomes an important process in the mercury sensitized reactions of the higher alkenes. While at least 90% of excited propene molecules split into allyl + H(35) perhaps 10% go to vinyl + methyl radicals(36). No molecular elimination of hydrogen occurs in the primary act.

The relatively weak β - C - C bond in 1-butene facilitates dissociation into allyl and methyl radicals(35) and at moderate pressures (15 - 200 mm.) it is about 1.3 - 1.6 times as probable as a primary C - H split.(37) α -Bond cleavage also takes place but according to Majer, Mile and Robb(38) it is a minor process. Although isomerization of 1-butene to 2-butene occurs(38) it is a minor process as discussed by Cvetanovic(37) and others(39). They concluded that butene-1 isomerizes to methylcyclopropane and not to butene-2. Cvetanovic and Doyle(37) assigned the following mechanism to two excited states being involved.

$$1\text{-}C_4H_8(So) + Hg\ 6(^3P_1) \longrightarrow C_4H_8\ (T_1{}^V) + Hg\ ^1So$$

$$\begin{aligned} C_4H_8\ (T_1{}^V) &\longrightarrow \text{Products} \\ &\longrightarrow (C_4H_8)\ * \end{aligned}$$

$$C_4H_8\ (T_1{}^V) + M \longrightarrow 1 - C_4H_8 + M$$

$$(C_4H_8)\ * \longrightarrow \text{Products}$$

$$(C_4H_8)* + M \longrightarrow \Delta\text{-}\ CH_3 + M$$

The initial energy transfer process presumably forms the vibrationally excited triplet state of 1-butene ($C_4H_8\ T_1{}^V$) which can then dissociate or rearrange into a second excited state $(C_4H_8)*$ which is possibly the vibrationally excited triplet state of methylcyclopropane. The reaction is good evidence for two excited states being involved as suggested earlier for ethylene.

Cis-trans isomerization is the major primary process in the reaction of Hg 6 $^3P_1$ atoms with either the cis or the trans butene-2. Thus on prolonged irradiation of the cis-isomer a 1 : 1 mixture of trans and cis results.(37, 39) This reaction may also occur through an intermediate vibrationally excited triplet state.

Mass spectrometric detection of the primary products formed in sensitized reactions in fast flow reactor shows that at low pressures both hydrogen atom and CH_3 radical cleavage occurs with cis-butene-2 but isomerization to the trans form is the major process.(40) Under similar conditions, the primary act of dissociation of isobutene is formation of β -methallyl radical and a hydrogen atom.(35)

Arai and Shida(41) investigated the mercury $^3P_1$ sensitized reactions of ethylene at 350°C. The major products with Hg $^3P_1$ atoms are the same as at 25°C and the kinetics of the reaction fit quite well the Cvetanovic mechanism.(33)

1.2.(d) The Mercury Photosensitized Decomposition of Nitrous Oxide

The mercury photosensitized decomposition of nitrous oxide has been studied by Manning and Noyes(42) in 1932, who found that when the reaction was allowed to go to completion, the products were nitrogen and mercuric oxide.

$$N_2O + Hg^* \longrightarrow N_2 + HgO$$

By studying the pressure change, they found out that although initially small pressure increases had been there but overall there was no pressure change. It was thought that the intermediate decomposition products may be other than nitrogen. Two primary processes were considered to be possible.

(a) $Hg\ 6\ (^3P_1) + N_2O \longrightarrow NO\ (^2\pi) + N\ (^4S) + Hg\ 6\ ^1So$

(b) $Hg\ 6\ (^3P_1) + N_2O \longrightarrow N_2\ (^1\Sigma) + O\ (^3P) + Hg\ 6\ ^1So$

Cvetanovic(43, 44) reinvestigated this reaction in 1955 and found that at small conversions the products were nitrogen and atomic oxygen in the ratio of 2 : 1. Due to the formation of mercuric oxide, there was a slight deficiency in the oxygen. The slight variation in the rate of formation of nitrogen in the system was attributed to the depletion of mercury vapour in the system and also to the formation of mercuric oxide which reduces the transparency of the cell windows. Cvetanovic also noted that in the presence of an oxygen consuming compound (alkane or alkene) no mercury depletion occured and mercuric oxide was absent. He also found that the rate of decomposition of nitrous oxide was identical to the rate of formation of nitrogen. He concluded that the primary process in the above reaction was reaction (b), i.e. in which the formation of oxygen atom and nitrogen molecule takes place. Spin conservation rules predict that the oxygen atoms formed should be in the triplet state. Formation of an electronically excited N_2O molecule and formation of an energy rich HgO molecules

$$Hg\ 6\ (^3P_1) + N_2O \longrightarrow Hg\ 6\ ^1So + N_2O\ *$$

& $$Hg\ 6\ (^3P_1) + N_2O \longrightarrow HgO\ * + N_2$$

were also a possibility, but both of these were ruled out by Cvetanovic for several reasons. The former was ruled out on spectroscopic grounds and also because the rate of decomposition is pressure independant and in the latter HgO * could not show the reactions attributed to triplet oxygen atoms in the Hg/N_2O system and also HgO is not formed in the presence of oxygen consuming compounds.

The above technique is widely used as the most convenient source of ground state oxygen atoms due to its several advantages as listed below.

1. The system can be used over a wide pressure range.
2. The nitrogen formed in the system can be easily measured, thus making it possible to calculate the number of oxygen atoms produced.
3. By changing the intensity of the incident radiation the rate of atom production can be easily controlled.
4. The absence of molecular oxygen is ensured.
5. Nitrous oxide is inert to oxygen atom and free radical attack under most conditions.

Although the quenching efficiency of nitrous oxide is only about half as large as that for olefins, nevertheless by using a large excess nitrous oxide, the quenching of mercury by olefins can be minimized.

1.2.(e) Monoisotopic Mercury Photosensitization:

The method of monoisotopic excitation has been developed not long ago. It was first demonstrated by Mrozowski(45) followed by Zuber,(46) McDonald and Gunning,(47) and Zelikoff et al.(48) Subsequently, the utility of this technique as a photochemical means of isotope separation and of determining the primary act in mercury sensitized reactions has been well demonstrated.(5, 6)

Under special conditions, it is possible to achieve monoisotopic excitation in natural mercury vapour by the use of an electrodeless mercury discharge source containing a single isotopic species. When one of the fragmentation products of the primary decomposition of the substrate combines with the sensitizer to form a stable compound of mercury, the method becomes a unique and indispensible means of obtaining information regarding certain fine details of the primary reaction mechanism.

Gunning$^{(6)}$ and his co-workers have used the technique to obtain information about the course of mercury sensitization in several systems. Natural mercury consists of seven stable isotopes, and the $\lambda = 253.7$ nm. resonance line consists of ten hyperfine components of varying intensities. By use of a resonance lamp containing only Hg^{202}, from which a single line is obtained, it is possible to excite that isotope alone in the reaction mixture. Radiation enters the reaction cell containing reaction mixture consisting of normal mercury and a substrate and is selectively absorbed only by the ^{202}Hg component of the mercury. The excited ^{202}Hg atom then initiates photosensitized reactions of the substrate which are followed by subsequently analyzing products and reactants for their isotopic distribution. (The mixture, and more especially the lamp, must be kept cool so that the width of the Hg^{202} line is not sufficient to overlap the absorptions of other isotopes).

If a product of the sensitized reaction contains mercury, it may have been formed in the primary step or in some secondary step: if the former, the product will show enrichment of the Hg^{202} isotope; if the latter, the Hg abundances will be normal. Calomel forming reactions are among those that have been studied by this technique. Mercury sensitized photolysis of HCl or of alkyl chlorides yields mercurous chloride as a product. Two possible routes can be envisaged:

$$Hg^* + RCl \longrightarrow HgCl + R \qquad (a)$$

OR

$$\begin{aligned} Hg^* + RCl &\longrightarrow Hg + R + Cl \\ Hg + Cl &\longrightarrow HgCl \end{aligned} \qquad (b)$$

The product HgCl contains, in fact, over 50% ^{202}Hg (natural abundance 29.8%) in some cases. Where RCl is hydrogen chloride, the product is enriched by 35%, thus suggesting that 35% of the reaction proceeds via reaction (a) and 65% via reaction (b).

Monoisotopic sensitization may offer a method for isotope separation. Mercuric oxide is formed on mercury sensitized photolysis of water. In the presence of butadiene (to supress secondary randomising reactions due to OH radicals) up to 95% pure $Hg^{202}O$ can be produced with Hg^{202} resonance lamp. Repetitive photolysis could yield Hg^{202} of high isotopic purity; the other isotopes should be equally amenable to separation.

Zuber(46) attempted to separate the isotopes of mercury by the isotopically specific mercury photosensitized reaction with oxygen. He obtained the evidence that both the unreacted mercury, and the mercury in the HgO product, differed isotopically from natural mercury, provided nitrogen was added to the substrate. The pure oxygen reaction, on the other hand, was found to be much less efficient from the standpoint of isotopic specificity.

The oxygen reaction reviewed by Gunning(50) in 1958 proceeds by two routes with the isotopically specific one being 1.9% of the other. The addition of butadiene results in the formation of 88 - 95% pure(41, 42,51, 52) $Hg^{202}O$ which represents the highest enrichment obtained to date in a single step monoisotopic photosensitization process. Significantly, also, the effect of nitrogen on the reaction is negligibly small(51), contrary to Zuber's claim(46). On a similar basis as that used for the water reaction, Desnoyer et al (51) postulated the formation of an activated complex molecule, $(Hg.O_2)^*$ in the primary step, which decomposes by subsequent quenching reactions to yield products. The two substrates, watervapour and oxygen, both have bond-dissociation energies which exceed the energy of the 6 $^3P_1$ state of mercury by about 20K J mol^{-1} - 25 kJ mol^{-1}. Therefore, dissociation in a simple energy transfer process would be of very low probability. The oxygen reaction, however, has generally been thought to lead to the formation of an excited oxygen molecule and the possibility of formation of an excited complex between an Hg 6 $^3P_1$ atom and an O_2 molecule had not been previously considered. A controversy has developed in the literature concerning the state of the energy rich oxygen molecule thought to be formed in the primary step. The kinetic evidence used in these arguments seems to be of doubtful validity. However, this would be discussed later when dealing with mercury photosensitized oxidations.

1.3. REACTIONS OF OXYGEN ATOMS (O^3P) WITH ALKENES

In this section, the reactions of oxygen atoms (O^3P) with alkenes are discussed briefly as they may be involved in the oxidation system in the present study.

1.3.(a) Hydrocarbon alkenes:-

Cvetanovic (15) studied the reactions of oxygen atoms with alkenes making use of the nitrous oxide technique for the production of excited oxygen atoms. He first studied the reaction with ethylene (53) and conclusion was reached that the primary process was a direct addition of an oxygen atom to the double bond to form an energy rich intermediate ("hot" adduct molecule) which then underwent further reactions. The products formed were carbon monoxide, hydrogen, several paraffins (CH_4, C_2H_6, C_3H_8, C_4H_{10}), aldehydes (CH_3CHO and some higher homologs) and small amounts of ethylene oxide and some other compounds. These were explained by a predominant primary split of the "hot" adduct into $.CH_3$ and $.CHO$

$$.CHO \longrightarrow CO + H \xrightarrow{C_2H_4} .C_2H_5 \xrightarrow{\text{radicals}} \text{paraffins}$$

$$\cdot C_2H_5 + CHO + M \longrightarrow C_2H_5CHO + M$$

Acetaldehyde could result from the combination of $.CH_3$ and $.CHO$ or from direct stabilization of the initial adduct. It was found that there was a slight pressure dependance of the yields of some of the products, CO decreasing and CH_3CHO and ethylene oxide slightly increasing with increasing pressure. This indicated "hot" precursors of very short life times.

When Cvetanovic (54-56) studied the reaction of oxygen atoms with the higher homologs of ethylene, much more definite information on the formation of hot adducts was obtained. In general, the major reaction products obtained were addition products for e.g. epoxides and carbonyl compounds. Fragmentation products were mainly carbon monoxide, acetaldehyde and ethane. He also noted that the amount of addition products increase and fragmentation products decrease with increasing pressure. This indicated hot molecules of short lifetimes.

When the epoxide and carbonyl compounds are formed, they possess excess energies of the order of 376 and 480 KJmol^{-1} respectively, as a result of the high exothermicities of these reactions. The pressures at which efficient removal of this excess energy by collisions will occur depend on the lifetimes of the 'hot' products with respect to their fragmentation. These lifetimes in turn will depend on the number of degrees of freedom and on the bond strengths of the weak bonds in the molecules formed. In the case of ethylene, the number of degrees of freedom is relatively small and predominant fragmentation takes place at pressures where the products from propylene and 1,3 butadiene are largely stabilized. In case of butenes and higher alkenes, the lifetimes are still longer.

The type of addition products formed with a number of alkenes are well known. The products consist of the epoxides and some isomeric carbonyl compounds. The formation of these products can be explained on the basis of the following points.

(i) Addition is nonstereospecific.

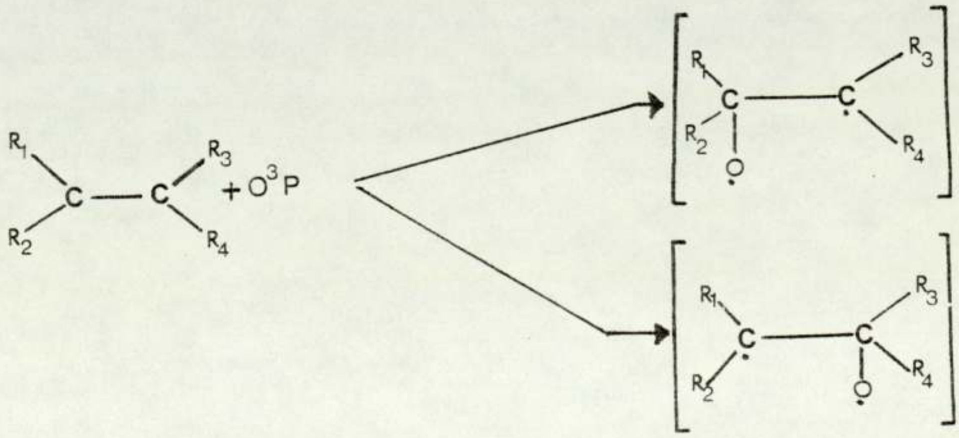
This is evident from the fact that with either of cis or trans butene-2 both cis and trans β butene oxides are formed.

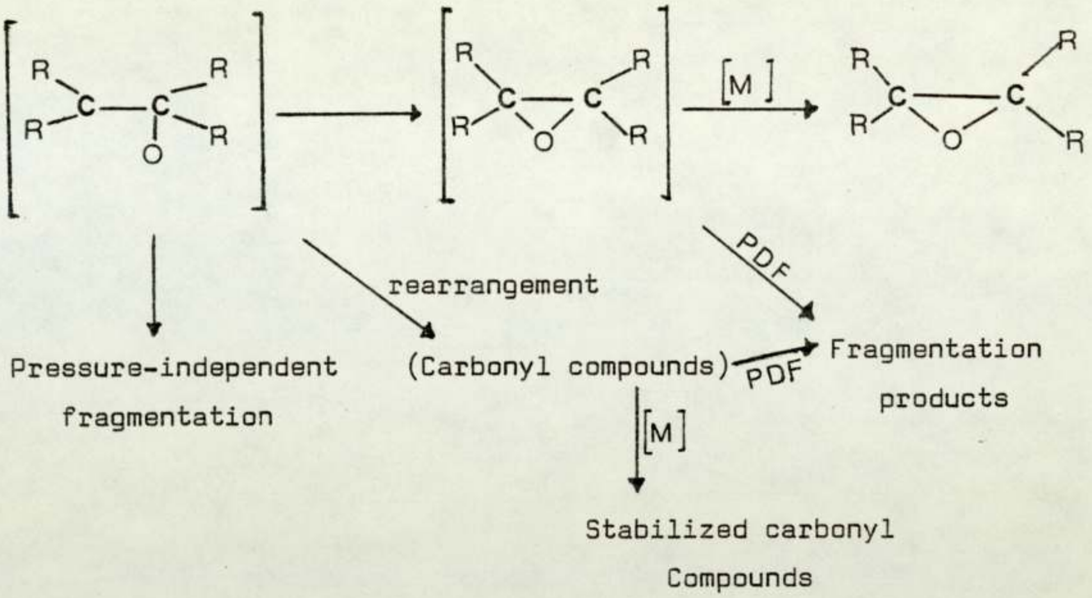
(ii) In unsymmetrical alkenes there is a pronounced orientating effect in addition.

(iii) Internal rearrangements occur in the initial biradicals to form carbonyl compounds.

(iv) The initially formed biradicals are probably very short-lived.

The results of Cvetanovic showed that the yields of addition products increased and those of fragmentation decreased when the pressure was increased in the system. This type of behaviour of the addition products is knows as "Pressure dependent fragmentation". The initial biradicals contain appreciable quantities of vibrational energy and they are capable of very rapid reactions along several paths. One of these paths is a "Pressure Independent Fragmentation", which occurs at high pressures where the fragmentation of the hot products is completely supressed. Fragmentation still takes place and the products are formed because the biradical is presumably very short-lived and does not experience a collision before partially decomposed by the pressure independent fragmentation route, as shown in the scheme below.





If the excess energy of the biradical is not removed by a collisional deactivation, it will be carried over to the "hot" addition products of the reaction. These "hot" products can be stabilized by collision and forms the observed addition products, that is to say epoxide and aldehyde at high pressures. If the pressure is kept low, most of energy is left behind with the adduct leading to a greater degree of fragmentation, some of the products decompose by the pressure dependent pathway.

The extensive study of the reactions of ground state oxygen atoms O^3P with olefins has revealed a number of general features about the reaction and its mechanism. They can be briefly summarized as follows.(15)

(1) Only addition to the double bond and no insertion into C-H bond occurs;

(2) The addition is non-stereospecific and is best explainable by assuming initial formation of a biradical intermediate;

(3) The biradical intermediate seems to be extremely short-lived (cis 2-butene and trans 2-butene do not give the same ratio of

cis and trans 2,3-epoxybutane) as its lifetime is comparable with the time of rotation around the original double bond.

(4) The biradical reacts unimolecularly in several ways:

(a) It is converted to "hot" epoxide by ring closure,

(b) It rearranges by internal migration of H atoms or alkyl groups into "hot" carbonyl compounds,

(c) It decomposes."Pressure-independent fragmentation" occurs.The biradical is too short lived to undergo collisional stabilization.

(5) The relative probability of reaction paths (a) - (c) in (4) is dependant on the energy content of the biradical when formed. Thus the pressure independent fragmentation has been observed to be more extensive at higher temperatures and probably also when the reacting oxygen atoms possess greater kinetic energy.

(6) The excess energy content of the biradical is carried over into "hot" products.

(7) The lifetimes of the "hot" products depend on:

(a) the number of degrees of freedom in the molecules and

(b) the bond strengths of the weak bonds in the molecules which undergo rupture.

(8) Ground state oxygen atoms exhibit an electrophilic trend in the rates of their addition to olefins.

(9) The trend in reactivity is almost entirely determined by differences in activation energies.

1.3.(b). Fluorinated Alkenes:

1. Reaction of oxygen atoms with perfluoro olefins:

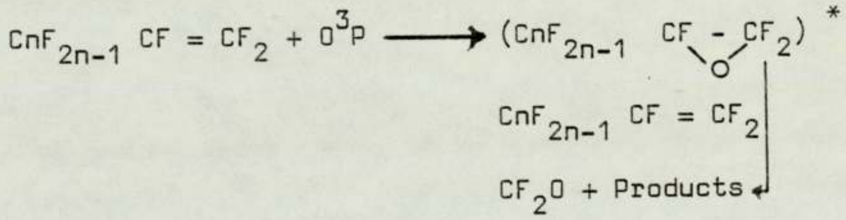
By studying the reaction of oxygen atoms with several perfluoro olefins(57 - 63) it is found that if the perfluoro olefin has a terminal double bond, the product is always carbonyl fluoride (CF_2O), that is to say

$$CnF_{2n-1}\ CF = CF_2 \ + \ \xrightarrow{O^3P} \ CnF_{2n-1}\ CF + CF_2O$$

The biradicals formed can

1. add to the original olefin,
2. cyclise or rearrange,
3. dimerise with another biradical.

The reaction scheme can be written as follows:



2. Reactions of oxygen atoms with partially fluorinated olefins:

The reaction of O^3P with halogenated 1,1-difluoroethylenes $CF_2 = CXY$ has been studied by Mitchell and Simons(64) using flash photolysis technique. They found that the oxygen atom adds to fluorinated carbon when X and Y are halogens, but to the other carbon if X and Y are hydrogens. The reaction products of halogenated 1,1-difluoroethylene was carbonyl fluoride.

$$CF_2 = CXY + O^3P \longrightarrow CF_2O + CXY$$

Some partially fluorinated alkenes behave much more like their corresponding unsubstituted alkene than the perfluoro alkenes. The reaction products of oxygen atoms obtained by mercury photosensitized decomposition of nitrous oxide with 2-trifluoromethyl propene (65) were found to be the epoxides and isomeric carbonyl compounds. The mechanism proposed for this addition reaction was analogous to the one proposed by Cvetanovic for the reaction of O^3P atoms with unsubstituted alkenes. This mechanism can probably be applied to most partially fluorinated alkenes but excluding those with fluorine substitution at the double bond. The alkenes with a fully fluorinated double bond behave similarly to the perfluoro alkenes.

In a similar study with 2-fluoro propene, Morley(66) found that the major products 2-fluoro propene epoxide and 2-fluoro propionaldehyde accounted for 90% of the oxygen atoms at pressures higher than 500 mm.

From both reactions, i.e. 2-trifluoromethyl propene and 2-fluoro propene, the oxygen appears to add to the less substituted carbon atom to form a biradical which can then cyclise to form the epoxide or rearrange to form the aldehyde.

Jones (67) in dealing with the reaction of O^3P atoms with 1,1,2-trifluorobutene-1 found that the major products of this reaction were cis- and trans-1-fluoropropene and carbonyl fluoride. Minor products were fluorocyclopropene, propionyl fluoride, ethane, ethylene and propane. No detectable epoxide was formed.

S. Rattanaphani (68) studied the reaction of O^3P atoms generated by mercury photosensitized decomposition of nitrous oxide with fluoroethylenes. She found that 1,2-difluoroethylene and trifluoroethylene reactions are mainly alike and form monofluoromethylene (CHF) radicals and carbonyl fluoride. The CHF radicals then added to fluoroethylenes form "hot" fluorocyclopropanes which could be stabilized by collision (or isomerize or fragment).

Moss and Jennings(69, 70) have measured the relative rate constants of the reaction of oxygen atoms with the fluorinated ethylenes and partly fluorinated propenes and butenes by using the nitrous oxide technique. They conclude that the rate of addition of oxygen atoms towards the fluoro-alkenes is decreased progressively with increasing fluorine atom in any position of the molecule. The only exception is that for C_2F_4, the rate constant is greater than ethylene itself.

Hence all the present information available indicates quite clearly that the reactions of oxygen atoms (O^3P) with a variety of alkenes in the gas phase are well understood.

1.4. PHOTOSENSITIZED OXIDATIONS WITH MOLECULAR OXYGEN

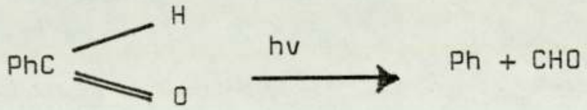
1.4.(a) Reactions in Solution:

A lot of work has been done in this area of photosensitized oxidations in the liquid phase. Most of the early work in this field is due to Schenck and his co-workers.(71)

Photo-oxidation is a reaction of molecular oxygen in the presence of light. It may take place as a direct process where a reactant absorbs the light or an indirect process where the light is absorbed by an added sensitizer, which then transfers its energy to reactants. The common sensitizers used in photo-oxidations are xanthenedyes, methylene blue, porphyrins, carotene, rubrene, chlorophyll, vitamin A, hypericin, polycyclic aromatic hydrocarbons and many other compounds.

The process of indirect or photosensitized oxidation can be further subdivided into two types.

(i) Type I process:- where the intermediates are free radicals formed as a result of absorption of light.



$$\mathrm{PhC(H){=}O \xrightarrow{h\nu} Ph + CHO}$$

(ii) Type II process:- where there are no free radicals but only electronically excited molecules occur as intermediates.

Dealing with the above processes the question arises whether the substrate or the oxygen is "activated" when it enters the termination reaction, which leads to the final product(s) AO_2 (where A is the substrate). Hence we may distinguish an acceptor-activation mechanism from an oxygen-activation mechanism. Furthermore, in each of these mechanisms the activated species may be either the electronically excited A or O_2 respectively or the electronically excited complexes of the primarily excited species with A or O_2 respectively (see Table 1.4.1.).

TABLE 1.4.1.(75)

DIRECT	INDIRECT (Photosensitized)
$A + h\nu \longrightarrow A^*$	$S + h\nu \longrightarrow S^*$
I. ACCEPTOR-ACTIVATION MECHANISM.	
$A^* + O_2 \longrightarrow AO_2$ (direct combination)	$S^* + A \longrightarrow S + A^*$ (Energy Transfer)
	$A^* + O_2 \longrightarrow AO_2$
$A^* + A \longrightarrow (AA)^*$ complex form:	$S^* + A \longrightarrow (SA)^*$ complex formation
$(AA)^* + O_2 \longrightarrow A + AO_2$	$(SA)^* + O_2 \longrightarrow S + AO_2$
II. OXYGEN-ACTIVATION MECHANISM.	
$A^* + O_2 \longrightarrow A + O_2^*$ (energy transfer)	$S^* + O_2 \longrightarrow S + O_2^*$ (energy transfer)
$O_2^* + A \longrightarrow AO_2$	$O_2^* + A \longrightarrow AO_2$
$A^* + O_2 \longrightarrow (AO_2)^*$ complex form:	$S^* + O_2 \longrightarrow (SO_2)^*$ complex formation
$(AO_2)^* + A \longrightarrow A + AO_2$	$(SO_2)^* + A \longrightarrow S + AO_2$

A = substrate, A^* = singlet or triplet excited A

$(AA)^*$, $(AO_2)^*$ = electronically excited complexes

S = sensitizer, S^* = singlet or triplet excited S

$(SA)^*$, $(SO_2)^*$ = electronically excited complexes

Livingston(72) has discussed type I and type II direct and indirect photo-oxidation reactions including their mechanistic aspects. Hochstrasser and Porter(73) have reported on the primary processes in photo-oxidation. Type II direct and indirect photo-oxidations of diene systems have been compiled by Gollnick and Schenck(74). Most of the work on alkenes as substrate in type II indirect photo-oxidations can be found in early papers of Schenck(71) and his co-workers, and recently it has been reviewed by K. Gollnick(75) and others.(76)

Gaffron(77 - 79) was the strong supporter of the acceptor activation mechanism and he showed that the quantum yields of the direct and indirect processes are independant of the intensity as well as of the exciting wavelength of light. He also observed that in the direct photo-oxidation of rubrene, two rubrene molecules have to take part in the reaction sequence, which leads to stable endoperoxide. He concluded the formation of an activated double molecule $(Ru_2)^*$ occured as shown below:

$$Ru^* + Ru \longrightarrow (Ru_2)^* \text{ ——— 1a}$$

(formation of activated double molecule (eximer formation)).

$$(Ru_2)^* + O_2 \longrightarrow RuO_2(\text{stable}) + Ru \text{ ——— 1b}$$

The same reaction was also studied by two other groups of investigators,(80 - 82) Schumacher (81) confirmed the participation of two molecules of rubrene in this reaction, however he postulated the formation of an unstable electronically excited rubrene oxygen complex which should either dissociate into its components or can be stabilized by collision with other rubrene molecule.

$$\mathrm{Ru^* + O_2} \longrightarrow \mathrm{RuO_2^*} \quad \text{————} \quad 2$$

$$\mathrm{(RuO_2)^*} \longrightarrow \mathrm{Ru + O_2} \quad \text{————} \quad 2a$$

$$\mathrm{(RuO_2)^* + Ru} \longrightarrow \mathrm{RuO_2 + Ru} \quad \text{————} \quad 2b$$

A variation was proposed by Schonberg(83) that the light absorber forms a labile complex with oxygen and then delivers its oxygen to a substrate forming the peroxide and the light absorber in the original state.

$$\mathrm{(Ru_aO_2)^* + Ru_b} \longrightarrow \mathrm{Ru_a + Ru_bO_2} \quad \text{————} \quad 2c$$

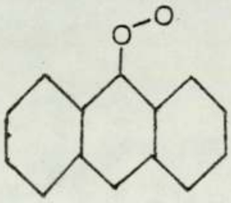
During the same time, Kautsky(84 - 88) while studying the extinction of fluorescence and phosphorescence by various quenchors assumed a mechanism quite contrary to the assumption of a sensitizer oxygen complex formation. He assumed that an energy transfer from an electronically excited molecule to oxygen occurs by which oxygen should be transferred from its triplet ground state into its electronically excited singlet state presumably into $^1\Sigma_g^+$ state(85, 86). Later on the $^1\Delta_g$ state of oxygen discovered in 1933(89) was discussed by Kautsky(88) as the low energy (92 KJ/mole) singlet oxygen formed in Gaffron's experiments. In the latter years, Gaffron's acceptor activation mechanism was almost omitted since the results obtained by different investigators(81, 90, 91) were only in agreement with an oxygen activation mechanism, however the nature of activated oxygen species remained obscure.

Schenck,(71, 90, 92 - 94) a major contributor to the field of photosensitized oxidation reactions, strongly advocated the view that the interaction between an electronically excited sensitizer and oxygen should result in a (chemical) addition reaction rather than in a (physical) energy-transfer reaction. He also found that the rate of disappearence of the active intermediate does not depend on sensitizer concentration.

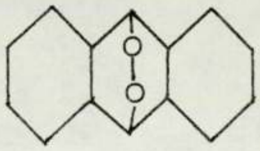
Until recently, the singlet oxygen mechanism was generally disregarded, despite the following observations:

1. Kautsky observed that reaction occurs even when sensitizer and acceptor are adsorbed on separate granules of silica gel, which would indicate that a reactive intermediate is formed which is capable of diffusion under vacuum.(85, 86) Similar phenomenon were noted by Rosenberg and Shombert.(95)

2. The "moloxide" would have to have an unexpected property, for example in the reaction with anthracene, which is both sensitizer and acceptor, the kinetics require that the intermediate (which, if it is a moloxide, is presumably of structure I) cannot collapse to product II itself, but must transfer oxygen to a second anthracene molecule.(76)



I



II

This represented a sharp change in the established views of the reaction. In 1964, very strong evidence in support of the mechanism involving excited oxygen was found by Foote and Wexler(76) and by Corey and Taylor(96), who showed that the typical products obtained from cyclic 1,3 dienes and olefins which could only be made by a photochemical reaction and were explained on the basis of excited light absorber-oxygen complex, were also obtained when excited singlet oxygen molecules, presumably $^1\Delta_g$, are reacted with substrates suitable for photo-oxidation reactions. Singlet oxygen may be generated either chemically or by electric discharge.(96, 97) Furthermore, Foote and his co-workers showed unequivocally that singlet oxygen oxidation and photo-oxidation give rise to the same product distribution in stereoselective reactions and that both oxidation reactions display the same kinetic features with different substrates. These results allow the conclusion that the photo-activated oxygen in the previous works is identical with the reacting species in Foote and Corey's experiments singlet oxygen.

Trozzolo and Fahrenholtz(98), in a recent study involving the ability of 2,5 diphenyl-furan endoperoxide, obtained by the sensitized photo-oxidation of 2,5 diphenyl furan, to transfer molecular oxygen to other oxygen acceptors such as tetramethyl ethylene, cyclohexadiene-1,3 and rubrene (all of these have been shown previously to react with singlet oxygen molecules to form characteristic products)(99, 71, 75) thought that if the evolving oxygen is in singlet state then this would form products with the above acceptors. In fact, they were confirmed in their results that the singlet oxygen mechanism applies to the oxygen transfer reactions of their compound 2,5 diphenylfuran endoperoxide.

Recently, Schenck has inferred that in the case of Type II photosensitized oxidations formation of singlet oxygen occurs by dissociation of excited sensitizer-oxygen complexes (Kautsky-Schenck mechanism).(100)

A novel variety of Kautsky-Schenck mechanism is described as formation and reaction of Kautsky exciplexes with O_2 forming sensitizer-O_2 exciplexes as intermediates of photo-oxidations and precursors of $^1O_2$. This complexolytic mechanism of $^1O_2$ formation is predominant under normal conditions, provided that

(i) sensitizer concentrations are high enough for efficient fluorescence self quenching, and

(ii) oxygen pressures are low enough (normal oxygen pressure) so that self quenching preceeds oxygen quenching.

Gollnick(101) et al., during their studies of photosensitized oxidations as a function of the triplet energy of sensitizers have concluded that their results so far obtained clearly indicate that only one oxidation species is involved in the photosensitized reactions in solution. This species they say is with all probability the singlet oxygen presumably in its $^1\Delta_g$ state produced from $^3(\pi, \pi^*)$ as well as from $^3(n, \pi^*)$-sensitizers independently of the energy of these triplet-excited sensitizers. The above authors have also said that in view of their results it seems rather unlikely that reactions of singlet oxygen in $^1\Sigma_g^+$ state produced from triplet-excited sensitizers by energy-transfer in solution have ever been observed. Their conclusion is in agreement with Ogryzlo's(102) results according to which the $^1\Sigma_g^+ O_2 \longrightarrow {}^1\Delta_g O_2$ transition is so effective that the rate constant for reactions with $^1\Sigma_g^+ O_2$ would have to be about 10^8 times larger than that for $^1\Delta_g O_2$ reactions in order to be competitive. Furthermore, their results(101) provide further evidence that a sensitizer-oxygen contact pair participation in the product forming step (9) (as shown in reaction sequence) is very unlikely. These two species, excited sensitizer-oxygen contact pairs and $^1\Sigma_g^+ O$ should, however, play important roles as precursors of $^1\Delta_g O_2$

in photosensitized oxidation reactions in solution.

Hence, by replacing the complex discussed by singlet oxygen, the following reaction scheme accounts well for the direct and indirect photo-oxidation reactions.

${}^1S_o + h\nu \xrightarrow{I_{abs}} {}^1S_1$ Absorption (1)

${}^1S_1 \xrightarrow{K_2} {}^1S_o + h\nu^1$ Fluorescence (2)

${}^1S_1 \xrightarrow{K_3} {}^1S_o$ Internal conversion (3)

${}^1S_1 \xrightarrow{K_4} {}^3S_1$ Inter system crossing (4)

${}^3S_1 \xrightarrow{K_5} {}^1S_o$ Inter system crossing (5)

${}^1S_1 + {}^3O_2 \xrightarrow{K_6} {}^1S_o + {}^1O_2$) Energy transfer and (6)

${}^3S_1 + {}^3O_2 \xrightarrow{K_7} {}^1S_o + {}^1O_2$) singlet oxygen formation (7)

${}^1O_2{}^1 \xrightarrow{K_8} {}^3O_2$ Deactivation (8)

${}^1O_2 + {}^1A_o \xrightarrow{K_9} {}^1(AO_2)_o$ Product formation (9)

with ${}^1S_o$, ${}^1S_1$ and ${}^3S_1$ = singlet ground state, excited singlet and triplet state of sensitizer S respectively.

${}^1A_o$ and ${}^1(AO_2)$ = singlet ground state of organic substrate A and product AO_2 respectively.

${}^3O_2$ and ${}^1O_2$ = triplet ground state and excited singlet state of oxygen, ${}^3\Sigma_g^-$ ${}^1\Sigma_g^+$ and/or ${}^1\Delta_g$ respectively.

1.4.(b). Nature of Singlet Molecular Oxygen:-

A considerable number of electronically excited states of oxygen atom and molecules are known to exist, and spectroscopic

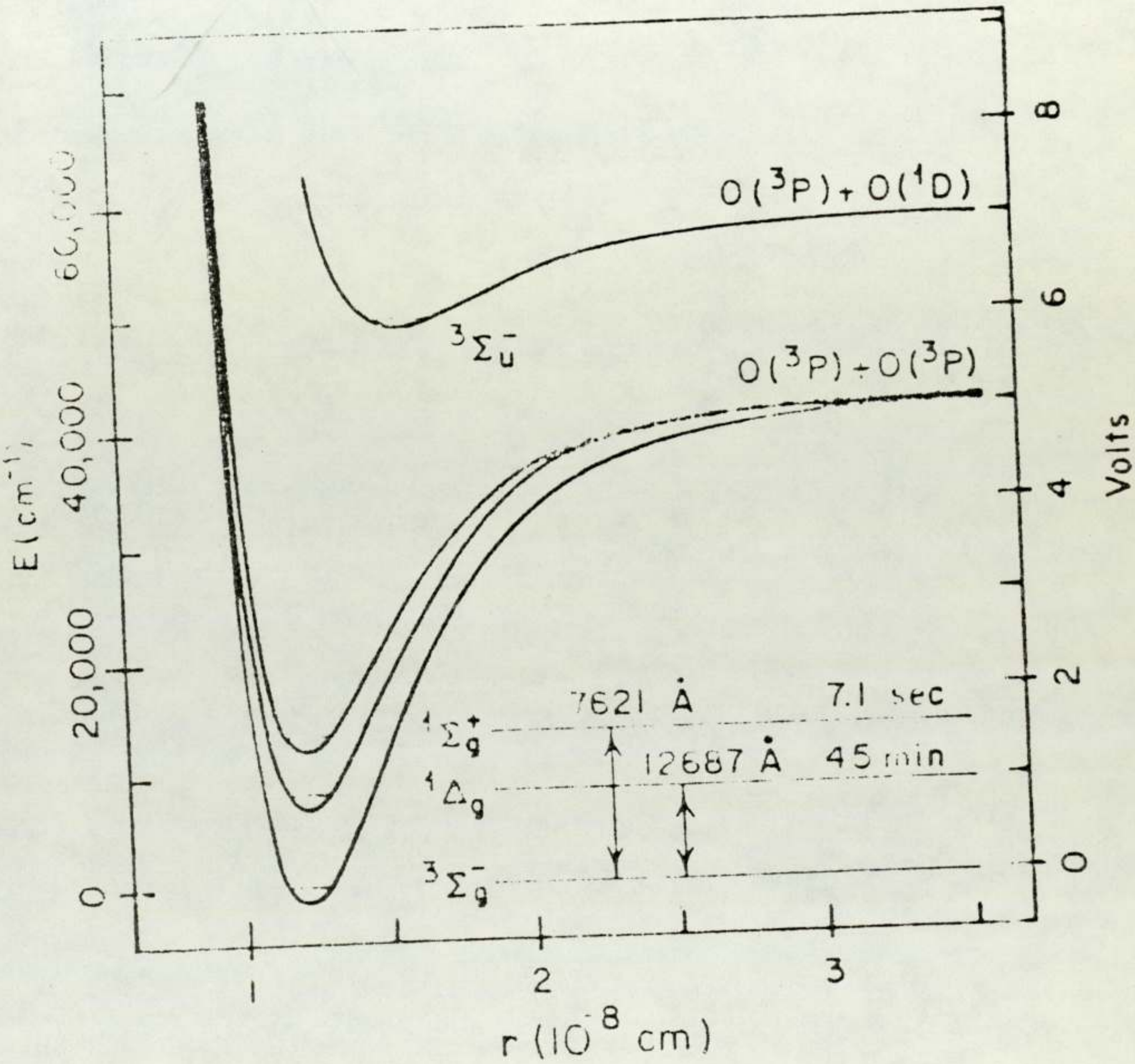

E (cm^{-1})
60,000
40,000
20,000
0
Volts
8
6
4
2
0
O(^{3}P) + O(^{1}D)
$^3\Sigma_u^-$
O(^{3}P) + O(^{3}P)
$^1\Sigma_g^+$
$^1\Delta_g$
$^3\Sigma_g^-$
7621 Å
7.1 sec
12687 Å
45 min
1
2
3
r (10^{-8} cm)

FIG. 1.4.b.1

data have provided detailed information about many of them. Several of these excited species are known to be involved in chemical reactions, either as reactants or as products. In contrast to most even electron molecules, the ground state of oxygen is a triplet spin state and the electronic metastable states are singlets. The ground state configuration of molecular oxygen is:

$$KK\,(\sigma_g\,2s)^2(\sigma_u\,2s)^2(\sigma_g\,2p)^2(\pi_u\,2p)^4(\pi_g\,2p)^2$$

and can give rise to the three state ${}^3\Sigma_g^-$, ${}^1\Delta_g$ and ${}^1\Sigma_g^+$
The ground state is ${}^3\Sigma_g^-$ and the states ${}^1\Delta_g$ and ${}^1\Sigma_g^+$ lie above it at 0.98 eV and 1.63 eV respectively. Both the singlet states, therefore, correlate with ground state, ${}^3P$, oxygen atoms.

Additional excited states are formed by the transfer of an electron from the bonding ($\pi_u\,2_p$) orbital to the antibonding ($\pi_g\,2_p$) orbital to give

$$KK\,(\sigma_g\,2s)^2\,(\sigma_u\,2s)^2\,(\sigma_g\,2p)^2\,(\pi_u\,2p)^3\,(\pi_g\,2p)^3$$

this would produce the states ${}^1\Sigma_u^+, {}^1\Sigma_u^-$, ${}^1\Delta_u$, ${}^3\Delta_u$ and ${}^3\Sigma_u^+$. ${}^3\Sigma_u^-$ dissociates into $O^3P + O^1D$, the rest all into ground state O^3P atoms.

The physical(103) data on three lowest electronic states of molecular oxygen reveal very small structural changes upon excitation as shown by the near consistancy of the internuclear distances. The potential curves for molecular oxygen reveal this by the near coincidence of the potential minima for the three lowest states (Fig. 1.4.b.1).

Transitions from ${}^3\Sigma_g^-$ to ${}^1\Delta_g$ is forbidden and similarly transition from ${}^3\Sigma_g^-$ to ${}^1\Sigma_g^+$ is also forbidden. A very strong transition comes from a triplet state ${}^3\Sigma_u^-$ and transitions from ${}^3\Sigma_g^-$ to this state is possible with 190 n.m. (628.0KJ) very high energy. Normally, it is not possible to obtain ${}^3\Sigma_u^-$ state especially with photosensitized reactions, hence the only two easily obtainable states by means of photosensitization are ${}^1\Delta_g$ and ${}^1\Sigma_g^+$ states.

The photosensitized generation of singlet molecular oxygen involves transfer of energy from an excited sensitizer molecule to normal molecular oxygen ${}^3\Sigma_g^-$. In a mechanism proposed as probably by Kawaoka(104, 119) and others, the triplet state of the sensitizer molecule is quenched, leaving the oxygen molecule in a singlet state (${}^1\Delta_g$ or ${}^1\Sigma_g^+$) after the collision. The excess energy of the sensitizer is left as the vibrational energy of the sensitizer.

$$\Delta_v = \Big[\Delta E\big(T - S_0\big)\Big] - \left[\Delta E \left\{ \begin{matrix} \left({}^1\Delta_g - {}^3\Sigma_g^-\right) \\ \left({}^1\Sigma_g^+ - {}^3\Sigma_g^-\right) \end{matrix} \right\}\right]$$

Energy transfer from triplet sensitizer to triplet oxygen to give singlet oxygen is a spin allowed process. The lowest states of oxygen are shown below with the electron distribution in the highest occupied (degenerate) orbitals.(105)

States of the oxygen molecule	Occupancy of highest orbitals		Energy above ground state
Second excited state (${}^1\Sigma_g^+$)	↑	↓	154.9 K J
First excited state (${}^1\Delta_g$)	↑↓	—	92.1 K J
Ground state (${}^3\Sigma_g^-$)	↑	↑	

The $^{1}\Delta g$ state has an energy only 92.1 K J $^{\text{mol -1}}$ above that of the ground state, both electrons are paired in a single orbital, leaving the other vacant. This state might be expected to undergo two-electron reactions; it resembles ethylene electronically, but should be more electrophilic. The higher singlet state ($^{1}\Sigma g^{+}$) resembles ground state oxygen electronically and might be expected to undergo one-electron free radical reactions. Both states have been identified spectroscopically as products of electrodeless discharge and of the chemiluminescent reaction of sodium hypochlorite and hydrogen peroxide,(97, 106) and at least one of the states is produced in certain other reactions.(107 - 109) The $^{1}\Delta g$ state has a much longer lifetime than the $^{1}\Sigma g^{+}$, and is the major product of the hypochlorite-hydrogen peroxide reaction.(97, 106)

1.4.(c). Formation of Singlet Molecular Oxygen.

(i) Chemical Methods:

1. Reaction(110, 111, 106) of hydrogen peroxide with hypochlorite or hypobromite. Quantitative(76, 112) yields of (probably) mainly $^{1}\Delta g$ with some equilibrium amounts of $^{1}\Sigma g^{+}$. Reaction yields enhanced by use of nonaqueous solvents (e.g. methanol).
2. Reaction(113) of potassium superoxide with water. Possibly a favorable source for $^{1}\Sigma g^{+}$ production.
3. Thermal decomposition(109) of arylperoxides. Probably favors $^{1}\Delta g$ production.

(ii) Physical Methods:

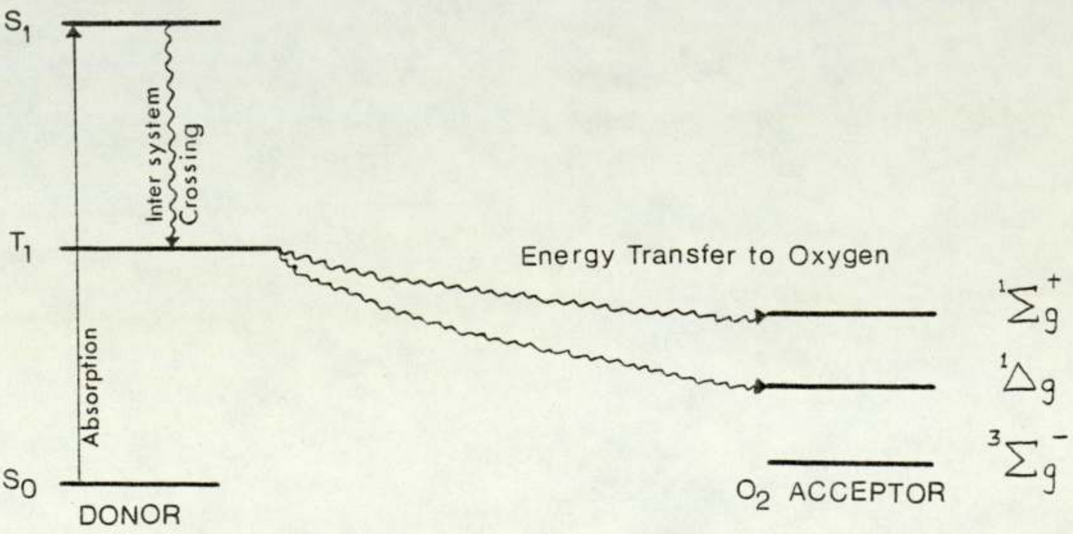
1. Photosensitization(99, 104, 114) by visible or near-ultraviolet light absorption, with excitation transfer to normal oxygen. Probably favors $^{1}\Sigma g^{+}$ with most sensitizers. Exclusively $^{1}\Delta g$ could be

produced with suitable infrared sensitizers. Uses ambient moderate light intensities with normal oxygen bubbled into irradiated reaction mixture.

2. Electrical discharge(97, 115 - 118) through a stream of gaseous oxygen. Stream of mainly $^1\Delta g$ bubbled into reaction solution after suitable scrubbing.

During the recent years, Kearns and co-workers(119) have calculated that in the region between about 155 - 205 K J mole^{-1} the ratio of formation of $^1\Sigma g^+$ and $^1\Delta g\ O_2$ is a function of the triplet energy of the sensitizers applied.(120) Sensitizers with triplet energies equal to or below 155 K J mole^{-1} produce $^1\Delta g\ O_2$, on raising the triplet energy to 205 K J mole^{-1} a smooth increase of $^1\Sigma g^+\ O_2$ occurs having a ratio of $^1\Sigma g^+ O_2 / {}^1\Delta g\ O_2$ to about 10. They suggest that low energy sensitizers like hematoporphyrin and methylene blue produce only $^1\Delta g\ O_2$ whereas high energy sensitizers such as eosin or fluorescein however produce about ten times as much $^1\Sigma g^+\ O_2$ as $O_2\ ^1\Delta g$.

A mechanism (as shown in the scheme below) for the production of singlet molecular oxygen by triplet energy transfer is proposed by Pitts.(121)



1.4.(d). Detection of Singlet Molecular Oxygen:-

Detection of the presence of singlet molecular oxygen in a system may be effected by direct physical observations if concentrations permit, or indirectly by the result of singlet oxygen reactions. Some useful detection methods are:

1. Luminescence Spectroscopy (110, 111, 115 - 117) Characteristic single-molecule transitions and double-molecule simultaneous transitions readily detected.

2. Mass spectroscopy (118) The presence of $^1\Delta g$ is monitored by O_2^+ appearance potential, the latter decreased relative to ground state O_2 by the transition energy $^1\Delta g \longleftarrow {}^3\Sigma \bar{g}$

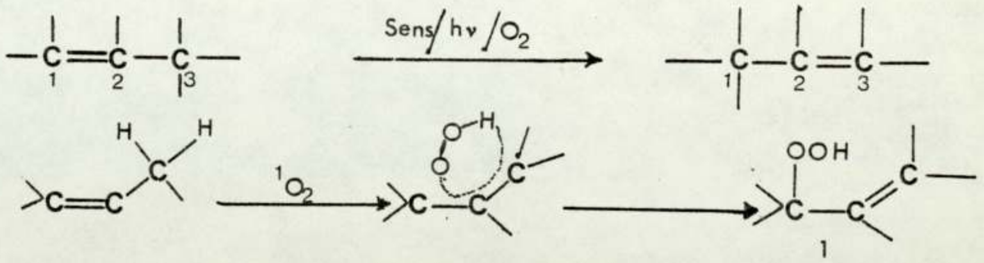
3. Chemical scavangers (96, 99, 122) Observation of characteristic products of singlet oxygen reaction.

1.4.(e). Dye Sensitized Oxidation of Alkenes:-

Dye sensitized photo-oxidation of alkenes, dienes, etc., proceeds via singlet oxygen formed by energy transfer from triplet sensitizer to oxygen. (75, 99) The dyes that sensitize photo-oxidations among them chlorophyll, is the most effective for organic substrates.

The typical product of dye sensitized oxidation of an ethylenic bond is an unsaturated hydroperoxide having the position of unsaturation moved one carbon atom away from the original ethylenic bond. These rearranged allylic hydroperoxides are the major oxidation products. (71, 75, 99) The process formally resembles the -ene reaction.

In 1943, Schenck discovered the photosensitized oxidation of alkenes which leads to the formation of α, β unsaturated hydroperoxides in which the double bond is shifted to the allyl position with respect to the starting material, according to the following scheme:



As oxygen displays the same features as e.g. maleic anhydride in the well known Alder reaction (-ene reaction)(123), this type of hydroperoxidation reaction was called indirect substitutive addition in the allyl position.(90) Schonberg(124) described this reaction as Schenck reaction. It occurs in three steps:

(i) Attachment of O_2 molecule to one of the carbon atoms of the double bond;

(ii) Shift of the double bond into the allyl position ($C_2 \rightarrow C_3$) and

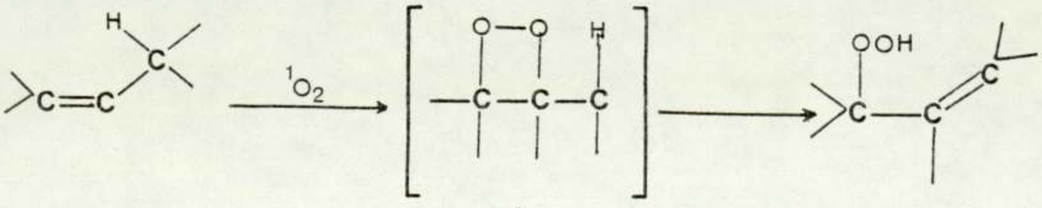
(iii) Migration of the allyl hydrogen atom to the terminus of the peroxy group.

The main features of this hydroperoxidation reaction are that in any case a shift of the double bond is connected with this reaction, and that no free radicals are involved; i.e. no hydrogen abstraction from the carbon atom α to the double bond occurs prior to the C - O bond formation, as is the case in auto-oxidation reactions.

In more recent investigations by Schenck et al.(125) on the photosensitized oxidation and on the auto-oxidation(126) of optically active olefins such as (+) limonene and (+) carvomenthene the differences between the two reactions have been revealed, thus ruling out any mechanism which assumes hydrogen abstraction to be the initiating process in the type II photosensitized hydroperoxidation reaction. The results also show that no insertion of the oxygen molecule into a C-H bond α to the double takes place, and that type II photosensitized oxidation reactions occur much faster with tri- and tetra substituted ethylenes than with di or mono substituted ones.(127, 128) The cis relationship between oxygen attack on a double bond and the migrating allyl hydrogen was shown by Nickon and Bagli(129, 130) that the allyl hydrogen taking part in the reaction has to be cis to the oxygen attack on the double bond.

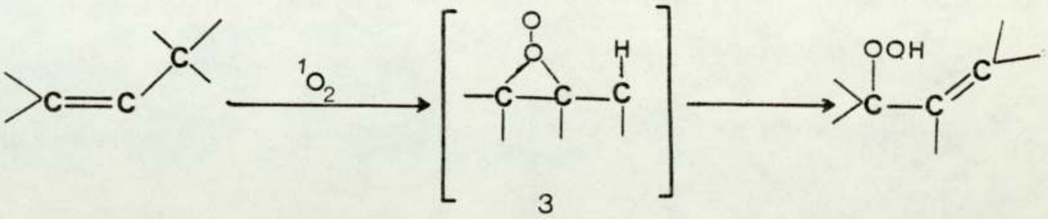
Until very recently, the above views seemed to be generally accepted. However, upon careful examination, the arguments used to support the above mechanism (-ene)(75, 99, 122, 130) and to eliminate other possible mechanisms seem less secure now, and there appear to be other schemes that deserve consideration.

Dioxetane intermediates (2) appear to be important in the formation of carbonyl containing products that are frequently observed in the reaction of conjugated olefins with singlet oxygen(131 - 133) and it is possible that they are also intermediates in the formation of allylic hydroperoxides according to the following scheme:



2

Perepoxides (3) have also been suggested as possible intermediates in the formation of the allylic hydroperoxides according to the following mechanism:(134)


3

Kearns and his co-workers have provided the experimental evidence for the presence of di-oxetane and perepoxide intermediates in singlet oxygen reactions with olefins, and at the same time provided strong evidence against the mechanism of the -ene reactions.(133, 135)

According to their theoretical considerations,(136) regarding the reactions of singlet oxygen with alkenes, simple mono alkenes such as methyl substituted ethylenes, perepoxide formation will be favored over dioxetane formation. Rearrangement of the perepoxide to a dioxetane or to an allylic hydroperoxide both appear to be possible (theoretically), although experiment indicates that the intramolecular abstraction reaction dominates. With those alkenes that have particularly low ionization potentials theory suggests that dioxetane formation will become more favorable. Their calculations also inferred that the reaction of singlet $^1\Delta_g$ oxygen with alkenes to form perepoxides intermediates is an allowed reaction, whereas the reaction to form dioxetane intermediates may or may not be allowed, depending upon whether the alkene has a sufficiently low π ionization potential.(136)

In subsequent studies involving the effect of substituents and solvents, the evidence points more in favour of the -ene mechanism, whereas the arguments supporting the alternative mechanisms seem less secure.(75, 136 - 139)

Ashford and Ogryzlo(140) took up a study on some reactions of singlet oxygen with olefins in the gas phase to obtain Arrhenius parameters for several -ene reactions in the gas phase so as to compare them with a few values already reported for the reaction in solution.(141) They arrived to several interesting points such as:

1. In the gas phase, the large variation in reactivity of the olefins (under study) can be attributed almost entirely to differences in activation energy. Within experimental error, these changes in activation energy for both the linear olefins and cyclic pentenes can be reproduced if it is assumed that:

   (a) the introduction of a methyl group reduces the activation energy by 6.2 K J mol^{-1}

   (b) one group cis to another causes a further drop of 3.3 K J mol^{-1}

   (c) a second pair placed cis to one another causes an additional drop of 1.2 K J mol^{-1}

   As many workers have pointed out,(75, 136, 139, 141) this rate accelerating effect of the methyl substituents is undoubtedly associated with the electron donating ability of this group and the electrophillic nature of singlet oxygen.

2. The room temperature rate constants in solution are about two orders of magnitude larger than those in the gas phase.

Since few reactions have been studied in both gas and condensed phase hence there are controversies over what differences should be expected. When either reactant is polar, differences have been observed.(142) However, when both reactants are not very polar, it would appear that there is usually very little change in the Arrhenius parameters when the medium is altered.

The authors(140) have further said that since in their studies where the reactants were also non-polar, the differences between the two phases could be taken as evidence for a polar transition state and they have cited following points in the favour of the above state.

1. A dioxetane intermediate appears very unlikely since all the available evidence points to the exclusive formation of carbonyl products from the decomposition of dioxetanes whereas the reactions under consideration produce hydroperoxides exclusively.

2. The -ene mechanism supposed a simple sixcenter cyclic intermediate analogous to that which is assumed in the conventional -ene reaction. Though the lack of a strong solvent effect has been used by Foote(143) to argue against other more polar intermediates, there is no reason to believe that the -ene transition state would not be somewhat polar in view of the strong electrophillic nature of $O_2\,{}^1\Delta_g$. Their data cannot be considered inconsistent with this mechanism.

3. The perepoxide intermediate was favoured by some 'azide trapping' experiments but later on it was discovered that the technique suffered from several complications and the results are inconclusive.(139) Their(140) data also proves against this intermediate. Kopecky and van de Sande(144) have also concluded that neither the perepoxides nor the 1,2 dioxetanes are

involved in the singlet oxygen reaction.

4. A charge transfer complex has been proposed for the analogous Diels-Alder reaction of singlet oxygen.(145) There is also some correlation between the ionization energies of the olefins and their reactivities. It is important to observe, however, that if no bound species exists and there is simply a charge transfer "interaction" in the transition state, the intermediate would be indistinguishable from that proposed in the -ene mechanism. On the other hand, a bound charge transfer complex seems much less likely. Electronic relaxation of $O_2\,{}^1\Delta g$ would probably be favored in such a complex unless the species were drawn together extremely strongly.(146) Since attempts to intercept(139) or isolate an intermediate at low temperatures(147) have been unsuccessful, such a possibility has little to recommend it at the moment.

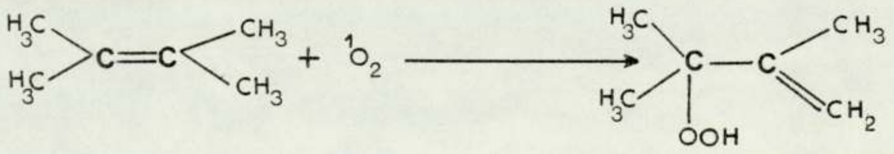
In the end, they have concluded(140) that a comparison of the same reactions in solution suggests a somewhat polar transition state is involved and in the absence of any evidence for a bound intermediate, this requirement can be accommodated by the simple -ene mechanism.

Type II direct and indirect photo-oxidation reactions with alkenes, etc., in solution are quite well understood now. Excited oxygen in the singlet state is with all the probabilities the oxidising agent in the reactions discussed. The mechanism by which it reacts with olefins and by which it is formed is receiving much attention. Many questions with regard to the mechanisms involved remain open, especially the effect of the nature of solvent on various processes is not fully understood at present. Intermediate singlet oxygen formation may also be important from a biological point of view and may plan an important role in air pollution. The photosensitized oxidation reaction can be used for the preparation of allylhydroperoxides and allyl alcohols. It may also be used for the preparation of certain organometallic hydroperoxides. The industrial use of singlet oxygen reactions is rather limited at the moment, but may be extended substantially in the years to come.

1.4.(f). Gas-phase reactions of $^1\Delta g\, O_2$ with Alkenes:-

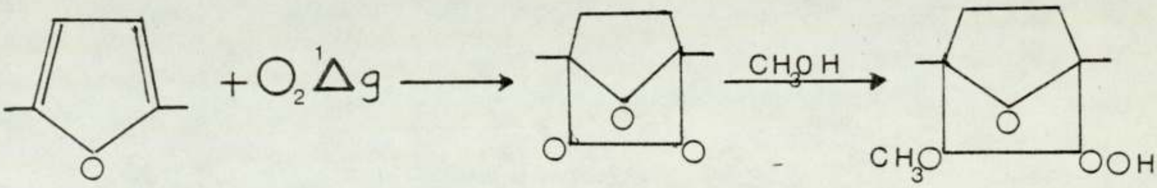
There is strong evidence that the excited O_2 (preferably in $^1\Delta g$ state) reacts with alkenes in solution, but the corresponding gas phase reactions have received little attention.

Wigner and Bayes$^{(148)}$ studied the kinetics of the decay of excited oxygen generated by the use of a microwave discharge in the presence of tetramethylethylene (TME) vapour. They identified the hydroperoxide as a product but did not measure the yield.



Corey and Taylor$^{(96)}$ however found no reaction between $O_2\ ^1\Delta g$ and TME in the gas phase. Similarly, Murray and Kaplan$^{(149)}$ mixed $O_2\ ^1\Delta g$ (obtained from a triphenyl phosphite-ozone complex) with TME vapour but their results were inconclusive.

Broadbent and co-workers(150) have observed the reaction of dimethylfuran and TME with excited oxygen produced through a microwave discharge. The presence of excited O_2 ($^1\Delta g$ or $^1\Sigma g^+$) in electrically discharged oxygen was first shown by the spectroscopic studies of Noxon.(151) Its survival in the oxygen stream outside the discharge was indicated by the mass-spectrometric study of Foner and Hudson.(152) The selective removal of oxygen atoms from such a system by the introduction of mercury into the discharge was described by Elias and others.(153) Coming back to the study of Broadbent et al.,(150) their results confirmed that both TME and DMF react with $O_2\,^1\Delta_g$ in the gas phase. Their results were further confirmed by a number of workers(154, 155) in more subsequent studies. The product from TME being a hydroperoxide and with DMF the unstable product formed in the reaction given below is an unstable pure ozonide (II) which on reaction with methanol gives the compound (III) whose properties were the same as those of an authentic sample.



Absolute rate constants for the above reactions were recently obtained by Broadbent, Gleason and Whittle, and are as follows:(155)

$$k_{TME} = 1 \pm 0.5 \times 10^5 \text{ litres moles}^{-1} \text{ sec}^{-1}$$
$$k_{DMF} = 3.7 \pm 1.4 \times 10^5 \text{ litres moles}^{-1} \text{ sec}^{-1}$$

As a comparison the rate constant for the reaction of ozone with TME is 4 x 10^4 litres $moles^{-1}$ sec^{-1}.(156) The rate constant for the reaction of TME with oxygen atoms is, however, very much faster than with either O_3 or $O_2\ {}^1\Delta_g$.

The above quoted rate constants were considerably smaller than Arnolds(102) preliminary estimation of 10^8 litres $moles^{-1}$ sec^{-1}. She investigated the removal of $O_2\ {}^1\Delta_g$ by a series of olefins.

Presumably all the olefins may react initially with $O_2\ {}^1\Delta_g$ to form hydroperoxides, although in view of the sensitivity of the hydroperoxides to surface decomposition as well as thermal instability and probably at low temperatures the very low yields might make it difficult to detect.(121)

Kummler(157) reports a private communication from Mahan which suggests that the rate constant for the reaction between $O_2\ {}^1\Delta_g$ and ethylene is slower, but not more than ten times slower than the reaction between atomic oxygen and ethylene. Thus the rate constant should be between about 2 x 10^7 and 2 x 10^8 litres $moles^{-1}$ sec^{-1}. Recently Herron and Huie(154) have examined the reaction rates of some of the alkenes with $O_2\ {}^1\Delta_g$ and have provided absolute rate constants for a number of alkenes and have compared them with those of atomic oxygen (Table 1.4.(f).1).

TABLE 1.4.(f).1 (154)

Rate Constants for some Reactions of O^3P and $O_2\,{}^1\Delta g$

Reactant	k(cm^3 mol^{-1} sec^{-1})		$kO^3P/kO_2\,{}^1\Delta g$
	O^3P	$O_2\,{}^1\Delta g$*	
Ethylene⊞(158 - 160)	4×10^{11}	1×10^7	4×10^4
Propene(58, 161, 162)	2×10^{12}	1×10^7	2×10^5
1-Butene (158, 162, 58)	2.5×10^{12}	1×10^7	2.5×10^5
2 Methyl Propene (158, 162)	1×10^{13}	-	-
2-Butene(158, 162)	1×10^{13}	1×10^7	1×10^6
2 Methyl-2-Butene (164)	4×10^{13}	1×10^7	4×10^6

* This work

⊞ References given are for kO^3P

There is no direct evidence for a reaction between $O_2\,{}^1\Sigma_g^+$ and alkenes although if it relaxes first to $O_2\,{}^1\Delta_g$ state rather than the ground state then the latter species would react with alkenes.(102) Khan and Kearns have shown that if there is a concerted addition of singlet oxygen across a double bond, then on the basis of the correlation diagram for the process, it can be predicted that only $O_2\,{}^1\Delta_g$ and not $O_2\,{}^1\Sigma_g^+$ will react. The prediction cannot apply if the process involves more than one additive stages.

1.5. MERCURY PHOTOSENSITIZED OXIDATIONS OF HYDROCARBONS

The mechanism of oxidations of hydrocarbons in the gas phase is quite complicated and difficulties usually arise in initiating the reaction at sufficiently low temperatures. The use of mercury photosensitization in a flow system helps to overcome most of the difficulties.

Although the field is quite old, in fact Marshall's(165) early experiments on mercury sensitized reactions of hydrogen and oxygen were conducted in the 1920's, but then Gray(166, 167) and Nalbandyan's(168, 169) experiments with alkanes were performed in the early 1950's, and then in the years to come oxidations were mostly performed with oxygen atoms involving this technique. Little attention was paid on mercury sensitized oxidations with molecular oxygen, probably because of the complications in the system where oxygen, ozone, and oxygen atoms are all present and reacting.

1.5.(a). Reaction of Excited Mercury with Oxygen:-

Molecular oxygen is an effective quenchor for the 253.7 n.m. mercury resonance line. The quenching cross section is large. Values in the literature vary in the range 1.32 - 1.99 n.m.(9, 11) Burgess and Robb(170) have adopted a value of 1.72 n.m. for $\sigma^2 O_2 \ H_g \ 6^3 \ P_1$. This quenching process involves the transition from the 6^3P_1 state of Hg to the $^1S_0$ state, a transition that occurs with an energy liberation of 4.88 ev or 469.7 K J mol^{-1}. The formation of ozone and HgO by the reaction of $Hg6^3P_1$ atoms and molecular oxygen was first reported by Dickenson and Sherrill,(171) but there was no certain information regarding the state of the oxygen molecules involved in the quenching collisions with $Hg6\,^3P_1$ atoms.

Leipunsky and Sagulin(172) and Dickenson and Sherrill(171) suggested that one of the reactions (1) or (2) may occur.

$$Hg\ 6\ ^3P_1 + O_2 \longrightarrow Hg\ O + O \quad \text{———————} \quad (1)$$

$$Hg\ 6\ ^3P_1 + O_2 \longrightarrow Hg + O_2^{*} \quad \text{———————} \quad (2)$$

Mercuric oxide has been observed as a product of the mercury photosensitization of oxygen-containing mixtures(166, 174 - 179) and in $Hg - O_2$ mixtures irradiated with 253.7 n.m. radiations(171, 180) but this may arise either from reaction (1) or from the reaction of mercury with a product formed as a result of reaction (2).

Volman(181) while studying the effects of foreign gases on the formation of ozone in the mercury sensitized reaction at 253.7 n.m. have suggested the following three processes for the deactivation of $Hg\ 6\ ^3P_1$ atom ultimately leading to ozone formation:

$$Hg\ 6\ ^3P_1 + O_2 \longrightarrow Hg\ 6\ ^1S_o + 2O\,^3P \quad \underline{\Delta H = 23\ KJ/mole} \ (1)$$

$$Hg\ 6\ ^3P_1 + O_2 \longrightarrow Hg\ O_{(g)} + O \quad \underline{\Delta H = -87 + \lambda} \quad (2)$$

$$Hg\ 6\ ^3P_1 + O_2 \longrightarrow Hg\ 6\ ^1S_o + O_2^{*} \quad \text{—————} \quad (3)$$

where λ is the heat of sublimation of $HgO_{(s)}$ estimated $< 96\ K\ J\ mol^{-1}$.

These reactions have been discussed by Volman(182) as follows:

Process (1) is sufficiently endothermic that only one collision in 10^4 may be effective, thus since the quantum yield of O_3 lies in the range 0.03(183) to 0.14(184) and chains are not involved reaction (1) must be unimportant.

While process (2) originally suggested by Leipunsky and Sagulin(172) is exothermic by at least 267.9 K J and is energetically possible, the extent depending on the value of the heat of sublimation (estimated 96.2 K J)(182), solid HgO is formed and mercury removed from the reaction zone. Further, if this were followed by

$$O + O_2 \longrightarrow O_3$$

there would be one ozone molecule formed from each mercury atom removed. It is claimed that from 7(171) - 60(181) molecules of ozone are formed per mercury atom entering the reaction zone hence this reaction cannot be important unless Hg is regenerated. Following reaction has been suggested.

$$HgO + O_2 \longrightarrow Hg + O_3 \qquad \Delta H = 68 - \lambda$$

However, if the heat of sublimation λ is 96.2 K J or less, as seems likely, then the above reaction will be highly endothermic and hence (2) seems an unlikely primary process. Furthermore, Volman(182) cites the fact that Pertel and Gunning(185) reported no isotopic enrichment in ^{202}HgO when the radiation source was a ^{202}Hg monoisotopic resonance lamp. This seemed to be a strong evidence against primary process (2) at that time.

The effect of foreign gases were studied in the mercury sensitized reaction at 253.7 n,m. and the direct photolysis at 184.9 n.m.(181, 183) The relative ozone yields drops in the order 1.0, 0.6, 0.6, and 0.4 for He, Ar, Ne and CO_2 and Volman suggested that the added gases deactivate the excited oxygen formed in primary process (3) before it can undergo the proposed secondary ozone generating reactions.

$$O_2^* + O_2 \longrightarrow O_3 + O$$

$$O_2^* + M \longrightarrow O_2 + M^*$$

$$O + O_2 + M \longrightarrow O_3 + M$$

$$O_3 + Hg \longrightarrow HgO + O_2$$

Since HgO is formed in a secondary process, no isotopic enrichment in ^{202}HgO would be expected. Thus Volman$^{(182)}$ concludes that (3) is the major primary process and notes that several possible states of the excited molecule have been proposed.$^{(186 - 189)}$ Callear, Patrick and Robb$^{(184)}$ also arrived at the same conclusion as Volmans and further added that since HgO was formed in a secondary process, hence reactions such as

$$Hg\ 6\ ^3P_1 + O_2 \longrightarrow HgO_2$$

$$HgO_2 + O_2 \longrightarrow HgO + O_3$$

can be excluded$^{(11)}$ and that (3) is the major primary process. They however could not speculate on the nature of energy rich oxygen molecule formed in process (3).

Various suggestions have been made in the later years regarding the controversy over the initial act of energy transfer.

Gunning and Strausz$^{(6)}$ reported that with $^{202}Hg\ 6\ ^3P_1$ sensitization of oxygen-butadiene mixtures, mercuric oxides containing 88 - 95% ^{202}Hg were recovered (which corrected an earlier false lead)$^{(182)}$. The result could have been interpreted in the favour of process (2), were it not for the fact that the relative ozone yields are reduced by the addition of inert foreign gases. This opens up the possibility of a process (4), the formation of the excited complex $(Hg.O_2)^*$

$$Hg\ 6\ {}^3P_1 + O_2 \longrightarrow (Hg.O_2)^* \text{ ——— } (4)$$

as it could lead to isotopic enrichment of the ultimate product HgO.

Oxygen is not the only compound capable of forming complexes with Hg 6 $^3P_1$ atoms of short duration. J.B. Homer(190) explains the rise in the rate of decomposition of certain compounds by excited mercury in the presence of carbon monoxide by the supposed existence of a $HgCO^*$ complex. G. Karl(191, 192) interprets the I.R. spectrum emitted by CO and NO in the presence of atomic mercury Hg 6 $^3P_1$ again by granting the existence of $HgCO^*$ and $HgNO^*$ complexes. M.Z. Hoffman(193) interprets the photodecomposition of ammonia by atomic mercury Hg 6 $^3P_1$ using the help of a $(Hg - NH_3)^*$ complex. Such complexes have never been shown by direct evidence.

The idea of forming an unstable excited species HgO_2^* in the primary process was originally proposed by Chen(194) in 1957 and was also advanced by Desnoyer et al.(195) It was supposed that the "complex" dissociates in a quenching reaction to form ozone and HgO. The quantum yield of ozone formation was thought to be 0.51 by Chen.(194) The situation is unresolved, but it would seem that the sequence

$$Hg\ 6\ {}^3P_1 + O_2 \longrightarrow (Hg.O_2)^*$$

$$(Hg.O_2)^* + M \longrightarrow Hg\ 6\ {}^1S_o + O_2 + M$$

$$(Hg.O_2)^* + O_2 \longrightarrow HgO + O_3$$

might be consistent with both the inert gas kinetic results of Volman and the isotopic enrichment studies of Gunning and Strausz.

The possibility of a process (5)

$$\text{Hg } 6\ {}^3P_1 + O_2\,{}^3\Sigma_g^- \longrightarrow \text{Hg } 6\ {}^3P_o + O_2^{\neq} \qquad (5)$$

in which the excited mercury atom is ought to be found in a lower energy level, i.e. the metastable state 6 ${}^3P_o$ rather than the 6 ${}^1S_o$ state and where $O_2^{\neq}$ is a vibrationally excited molecule is rejected by Callear and Williams(196) who have shown that molecular oxygen does not deactivate mercury Hg 6 ${}^3P_1$ to Hg 6 ${}^3P_o$. Their view was further supported by a recent study of Morand and Nief(197) who were considering the possible deactivation processes of Hg 6 ${}^3P_1$ by molecular oxygen. From their study of the oxidation of mercury in the mixtures Hg + O_2 and Hg + O_2 + butadiene illuminated by photons of 253.7 n.m. from a monoisotopic mercury (^{202}Hg) lamp, they arrived to the conclusion that two possible deactivation processes of Hg 6 ${}^3P_1$ by molecular oxygen should be considered.

The most important process is the direct energy transfer to the oxygen molecule,

$$\text{Hg } 6\ {}^3P_1 + O_2\,{}^3\Sigma_g^- \longrightarrow \text{Hg } 6\ {}^1S_o + O_2^*({}^1\Sigma_u^-)$$

the second process leads to the formation of an excited complex.

$$\text{Hg } 6\ {}^3P_1 + O_2\,{}^3\Sigma_g^- \longrightarrow (\text{Hg}.O_2)^*$$

$$(\text{Hg}.O_2)^* \longrightarrow \text{Hg } 6\ {}^1S_o + O_2$$

The results obtained show the value of cross section for the formation of the complex $(\text{Hg}.O_2)^*$ to be of the order of 0.25 Å^2 . This gives a very strong support for the processes (3) and (4).

Accumulating all the possible processes of deactivation of Hg 6 ${}^3P_1$ atoms by molecular oxygen, one can speculate that only processes (3) and (4) seem to be consistent with the results so far obtained in the literature.

$$Hg\ 6\ {}^3P_1 + O_2 \longrightarrow Hg\ 6\ {}^1S_o + 2O^3P \text{ ——— } (1)$$

$$Hg\ 6\ {}^3P_1 + O_2 \longrightarrow HgO + O^3P \text{ ——— } (2)$$

$$Hg\ 6\ {}^3P_1 + O_2 \longrightarrow Hg\ 6\ {}^1S_o + O_2^* \text{ ——— } (3)$$

$$Hg\ 6\ {}^3P_1 + O_2 \longrightarrow (Hg.O_2)^* \text{ ——— } (4)$$

$$Hg\ 6\ {}^3P_1 + O_2 \longrightarrow Hg\ 6\ {}^3P_o + O_2^{\neq} \text{ ——— } (5)$$

Various suggestions(186 - 189) have been made regarding the state of the oxygen molecule in the process (3).

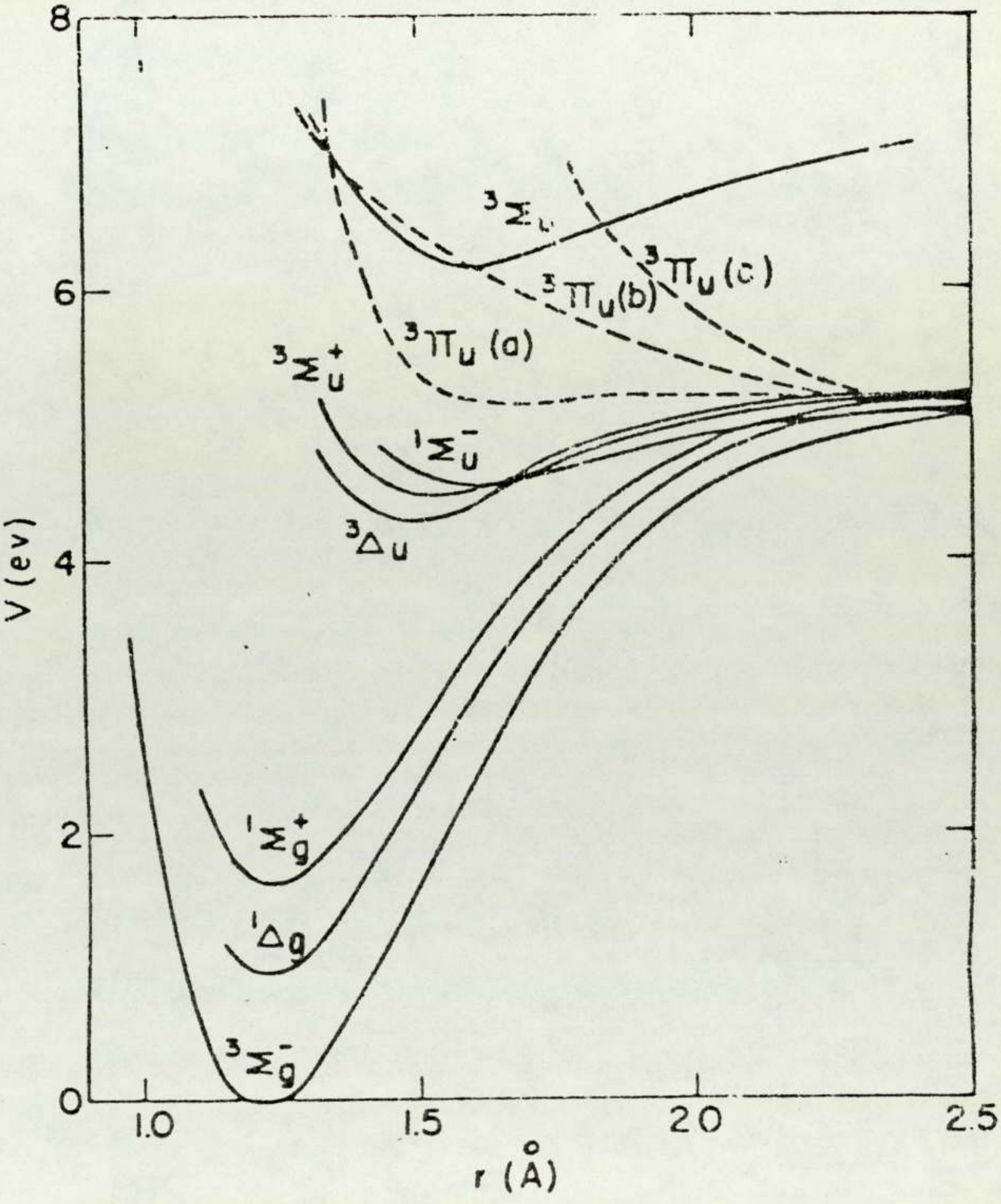
$$Hg\ 6\ {}^3P_1 + O_2\ {}^3\Sigma_g^- \longrightarrow Hg\ 6\ {}^1S_o + O_2^* \quad (4.88\ ev)$$

According to the correlation rules, possible complexes from Hg 6 $^3P_1$ and $O_2\ {}^3\Sigma_g^-$ allow transitions to any of the stable O_2 states arising from two O^3P atoms. The transitions are also allowed energitically as the 4.88 ev available at 253.7 n.m. is above the minimum necessary to reach any of these states.(189)

Mitchell(188) suggested that since the ground state of oxygen has a vibrational level at 4.86 ev, which corresponds closely to the energy released, this state will actually be formed; in other words, the electronic energy of the mercury will pass almost entirely into the vibrational energy of the oxygen. Laidler(198) points out the possibility of mercury sensitized photoexcitation in a spin allowed energy exchange process.

$$Hg\ 6\ {}^3P_1 + O_2\,{}^3\Sigma_g^- \longrightarrow Hg\ 6\ {}^1S_o + O_2\,{}^1\Sigma_g^+$$

In a subsequent paper, Laidler(189) suggested that state would be the one that should be produced, since in involves the least loss of electronic energy.



8
6
4
2
0
V (ev)
1.0
1.5
2.0
2.5
r (Å)
$^3\Sigma_u$
$^3\Pi_u(c)$
$^3\Pi_u(b)$
$^3\Pi_u$ (a)
$^3\Sigma_u^+$
$^1\Sigma_u^-$
$^3\Delta_u$
$^1\Sigma_g^+$
$^1\Delta_g$
$^3\Sigma_g^-$

FIG. 1.5.a.1

Volman$^{(181)}$ concluded from his earlier work that the O_2 is in a vibrationally excited $^1\Sigma_g^+$, $^1\Delta_g$ or $X^3\Sigma_g^-$ state (Fig. 1.5.(a).1). This conclusion was based on the fact that the ozone production was increased by the presence of foreign gases, the order of effectiveness being He > Ar > N_2 > CO_2. Volman argued that in order to explain the difference in production of ozone between added He and Ar, the O_2^* had to be formed in a highly excited vibrational state (either $^1\Sigma_g^+$, $^1\Delta_g$ or $X^3\Sigma_g^-$) so that the results could be explained by the difference in rates of vibrational deactivation. If the O_2^* corresponded to any of the highly excited electronic states in particular the $^3\Sigma_u^+$ then it is difficult to explain the relative effects of the added He and Ar. He did not consider the $^3\Delta_u$ or $^1\Sigma_u^-$ states, but the same arguments would hold for these states.

Gill and Laidler$^{(189)}$ however argued that if O_2^* were formed in a high vibrational level, the foreign gases would readily cause vibrational deactivation, and no overall increase in rate would be observed which they felt was evident from an analysis of Volman's experiments. To account for the effect of foreign gases, they concluded that their major role was on the reaction given below:

$$O + O_2 + M \longrightarrow O_3 + M$$

and that the order of effectiveness was:

$$He > Ar > N_2 > CO_2$$

There is abundant kinetic evidence that this is extremely unlikely.

Another argument used by Gill and Laidler$^{(189)}$ was that the most probable mechanism for (3) is one involving the least loss of total electronic energy. According to them, the $^3\Sigma_u^+$ state satisfies this requirement.

An attempt was made by Volman, Gill and Laidler(186) to resolve these conflicting arguments in a subsequent paper. They mentioned that the original work of Volman(181) could be misinterpreted because of the possibility that the concentration of Hg $^3P_1$ is greater at the higher flow rate, this effect being more or less independant of the flowing gas. Although they could not explain the relative effects of He and Ar but suggested that the $^3\Sigma_u^+$ state may still be the one involved.

An adequate explanation based on the potential energy curve determinations of various states of O_2 was made by J. Fallon, Vanderslice and Mason(187) (Fig. 1.5.(a).1). These authors point out that the curves for both the $^1\Delta g$ and $^1\Sigma_g^+$ states cross the curve for the $^1\Sigma_u^-$ state. The first crossing occurs at 4.96 ev above the lowest vibrational level of the $^3\Sigma_g^-$ state and the second at 4.88 ev. Both of these crossing points are uncertain by about ± 0.1 ev but analysis indicates that the curves do cross.

They point out that in addition to least net loss of electronic energy, a transition to one of the upper electronic states is more probable according to Franck Condon principle, since much less change in internuclear distance would be necessary and assuming that the transition is indeed to one of the states $^3\Sigma_u^+$, $^1\Sigma_u^-$ and $^3\Delta_u$ a radiationless transition to one of the low lying electronic states is possible. Both the $^1\Sigma_g^+$ and $^1\Delta g$ curves cross the $^1\Sigma_u^-$ curve at an energy around 4.9 ev, above the lowest vibrational level of the $^3\Sigma_g^-$ state. A pressure induced radiationless transition from the $^1\Sigma_u^- \longrightarrow {}^1\Delta g$ state is permitted, but the transition

${}^1\Sigma_u^- \rightarrow {}^1\Sigma_g^+$ is forbidden by the + $\not\leftrightarrow$ - rule.

In order to explain the effect of foreign gases, the molecules must get from any of the states ${}^3\Sigma_u^+$, ${}^1\Sigma_u^-$, ${}^3\Delta_u$ over to the ${}^1\Delta_g$ state via the ${}^1\Sigma_u^-$ state since it is the only one crossed. This can happen if the initial transition goes directly to the ${}^1\Sigma_u^-$. It can also happen if the initial transition is to the ${}^3\Delta_u$ and then the two pressure induced steps occur ${}^3\Delta_u \longrightarrow {}^1\Sigma_u^- \longrightarrow {}^1\Delta_g$. These transitions are permitted by Zener's$^{(199)}$ rule but the transition ${}^3\Sigma_u^+ \longrightarrow {}^1\Sigma_u^-$ is not because of + $\not\leftrightarrow$ - rule. Also the ${}^3\Sigma_u^+$ state can be definitely excluded as it reacts with ground state O_2 to give O_3 with a quantum yield of $2^{(198)}$ whereas from mercury sensitization ϕ (O_3) is only $0.03^{(183)}$ - $0.14^{(184)}$. Hence, of the three upper states the ${}^3\Delta_u$ or the ${}^1\Sigma_u^-$ are the most likely ones involved in the reaction, with the ${}^1\Sigma_u^-$ being the most probable since it has a vibrational level lying exactly 4.88 ev above the lowest vibrational level of the ${}^3\Sigma_g^-$ state$^{(200)}$. Another reason for the ${}^3\Delta_u$ state to be less important than the ${}^1\Sigma_u^-$ is that in the region where one might expect the transition ${}^3\Delta_u \longrightarrow {}^1\Sigma_u^-$ to occur, the nuclei are moving quite rapidly making the transition less likely.$^{(201)}$ Also the formation of ${}^1\Sigma_u^-$ rather than ${}^3\Delta_u$ appears more probably, since the Wigner Spin Conservation rule would favour the formation of a singlet rather than a triplet oxygen state to conserve total spin.$^{(11)}$

Therefore, either the formation of ${}^3\Delta_u$ or ${}^1\Sigma_u^-$ by energy transfer from Hg 6 ${}^3P_1$ could result in the formation of ${}^1\Delta_g$ O_2 in a high vibrational level. This interpretation could satisfy the arguments of Gill and Laidler that a high lying electronic state is initially formed, and at the same time it would satisfy the argument of Volman that the foreign gases affect a vibrationally excited low lying electronic level.

Finally, Heicklen$^{(203 - 205)}$ in his studies strongly supports the ${}^1\Sigma_u^-$ state of O_2 to be the one formed in the deactivation of excited Hg 6 ${}^3P_1$ by molecular oxygen. He points out that the excited molecule in process (3) must contain sufficient energy to react with an unexcited O_2 to produce O_3 and oxygen atoms some of the time. Thus the ${}^1\Sigma_g^+$ and ${}^1\Delta_g$ states are eliminated unless they contain a large excess of vibrational energy. However, if this were the case, O_2^* should be vibrationally deactivated rather efficiently by collision, contrary to the findings of Heicklen and Johnston.$^{(205)}$ Furthermore, the Franck Condon rules tend to favour the formation of electronic levels with small amounts of vibrational energy. All the transitions between ground state O_2 and the energetically accessible states are optically forbidden. The mercury induced transition permits the optically forbidden transitions. If this is the only optical selection rule which is relaxed then ${}^1\Sigma_u^-$ is the only permitted product state. This interpretation is consistent with the studies of the mercury photosensitized oxidations of per fluoro olefins.$^{(203 - 205)}$ However, the state cannot be completely ruled out. Morand and Nief$^{(197)}$ have also considered the ${}^1\Sigma_u^-$ state to be the one involved.

1.5.(b). Hydrocarbon Oxidation:

As previously said, most of the early work on mercury photosensitized oxidation of hydrocarbons with molecular oxygen have been carried out by Gray and Nalbandyan$^{(166 - 169)}$.

Nalbandyan's(168, 169) experiments were conducted at high relative oxygen concentration and at temperatures up to 310°C. He concluded that peroxides were the initial products and that conditions could be reached such that they were the only products of the reaction. He suggested a mechanism involving the formation of free radicals by the action of excited mercury on the hydrocarbon, which reacted with oxygen to give peroxy radicals, thus resulting in a chain reaction. At long contact times, the peroxides decomposed to form aldehydes, which then either decomposed or were oxidised to CO and CO_2. The peroxides were not identified but the aldehydes were found to be formaldehyde and acetaldehyde in the ratio of about five to one. Previous to Gray's experiments, no-one had isolated or identified the peroxides. Gray's expts. confirmed that peroxides were the only primary products and also showed that ethyl hydro peroxide was the only peroxidic substance produced in the initial stages of oxidation of ethane. Similarly, he obtained considerable amounts of methyl hydroperoxide in the photosensitized oxidation of methane. On contrary to Marshall, he mentioned that absence of detectable amounts of water or hydrogen peroxide in the product indicates that at the temperatures used, hydrogen atoms are removed by way of

$$H + O_2 \longrightarrow HO_2^* \longrightarrow H_2O \text{ or } H_2O_2$$

and that radical recombination or abstraction of hydrogen from ethane is of greater importance. The proposed mechanism is as follows:

$$Hg\ 6\ {}^1S_0 + h\nu \longrightarrow Hg\ 6\ {}^3P_1$$

$$Hg\ 6\ {}^3P_1 + RH \longrightarrow Hg\ 6\ {}^1S_0 + R + H$$

$$R + O_2 \longrightarrow RO_2$$

$$RO_2 + RH \longrightarrow ROOH + R$$

The course of the reaction is in general similar to that proposed by Bateman and Gee(206) in the photochemical oxidation of alkenes and was modified later on by Watson and Darwent(207) who explained the low yields of peroxide obtained in the ethane oxidation by suggesting the following reaction:

$$RO_2 + HO_2 \longrightarrow ROOH + O_2$$

They pointed out that the chain mechanism proposed by Gray would have to be of considerable length if the quantum yield was to be unity, since oxygen has a far smaller quenching cross section than ethane. Unfortunately, neither of the previous investigators determined the quantum yield. Watson and Darwent also showed that the quantum yield was $0.5 \longrightarrow 0.75$ and independent of intensity temperature, pressure, and composition at 40 - 80°C. Both of these findings are against the occurence of chains.

Burgess and Robb(170) in their experiments on mercury photosensitized oxidation of hydrocarbons, proposed that the rate of oxidation of the straight chain paraffins is found to be independant of pressure, while the other hydrocarbons show a dependence on the hydrocarbon pressure. This is interpreted as evidence for two types of chain reaction, the normal paraffins being oxidized by an "aldehyde" chain and the remainder by a "hydroperoxide chain". They say that the initial step involves the production of a radical R by the action of the products of of photosensitized oxidation on the hydrocarbon. Oxygen molecule adds to this radical to produce a peroxy radical, the nature of which determines the next step in the oxidation. In general, two types of reaction are possible, either the radical may abstract a hydrogen atom from the parent hydrocarbon to produce a hydroperoxide

$$RO_2 + RH \longrightarrow ROOH + R$$

$$R + O_2 \longrightarrow RO_2$$

or it may decompose, liberating a hydroxyl radical and an aldehyde or ketone. They have also said that the peroxides and hydroperoxides observed in previous works probably arise from non-chain reactions of the type

$$RO_2 + HO_2 \longrightarrow ROOH + O_2$$

and $$RO_2 + RO_2 \longrightarrow ROOR + O_2$$

There is a possibility that the peroxy radical formed

$$R + O_2 \longrightarrow RO_2$$

when R is small (e.g. methyl) may contain sufficient excess energy to undergo reactions which would not normally occur. Bell and McDowell(208) also supported Burgess and Robb's(170) view that the peroxide is formed in the reaction

$$RO_2 + HO_2 \longrightarrow ROOH + O_2$$

They studied the mercury photosensitized oxidation of isobutane(208) using a static system. There was a slow removal of mercury vapour ($\phi = 6 \times 10^{-4}$ at $30^{\circ}C$ and 2×10^{-4} at $100^{\circ}C$). The main product was t-butyl hydroperoxide together with smaller yields of t-butyl alcohol, acetone, methyl alcohol, formaldehyde and isobutyraldehyde.

There was no indication of a peroxide chain, the yields being below unity and independent of pressure, of a fixed hydrocarbon-oxygen mixture. Following mechanism was proposed by them.

$$RH^* \longrightarrow R + H$$

$$R + O_2 \longrightarrow RO_2$$

$$H + O_2 \longrightarrow HO_2$$

$$HO_2 + RO_2 \longrightarrow ROOH + O_2$$

They also suggested that since the yields of peroxide which is formed in the main terminating reaction ($HO_2 + RO_2 \longrightarrow ROOH + O_2$) increases with the increasing role of hydrocarbon in the excited mercury quenching processes, hence suggesting that the reaction between an excited hydrocarbon molecule and

$$RH^* + O_2 \longrightarrow R + HO_2$$

oxygen is important in the initiation process. Low peroxide yields for the oxygen-isobutane = 10 : 1 mixtures are attributed to a low efficiency of reaction, as shown below:

$$O_2^* + O_2 \longrightarrow O_3 + O$$

They have proposed a detailed mechanism for the oxidation of hydrocarbons through mercury photosensitization.

When mercury is illuminated by 253.7 n.m. radiation, the excited mercury atom may be quenched by either oxygen or the hydrocarbon.

$$Hg\ 6\ {}^3P_1 + RH \longrightarrow Hg\ 6\ {}^1S_o + RH^* \text{ ———— (a)}$$

$$Hg\ 6\ {}^3P_1 + O_2 \longrightarrow Hg\ 6\ {}^1S_o + O_2^* \text{ ———— (b)}$$

The excited hydrocarbon molecule may be deactivated,decompose, or react with oxygen.

$$RH^* \longrightarrow R + H \text{ ——— (c)}$$

$$RH^* + M \longrightarrow RH + M \text{ ——— (d)}$$

$$RH^* + O_2 \longrightarrow R + HO_2 \text{ ——— (e)}$$

For O_2^* the following sequence of reactions is given:

$$O_2^* + O_2 \longrightarrow O_3 + O \text{ ——— (f)}$$

$$O_3 + RH \longrightarrow RO + HO_2 \text{ ——— (g)}$$

$$RO + RH \longrightarrow ROH + R \text{ ——— (h)}$$

$$RH + O \longrightarrow R + OH \text{ ——— (i)}$$

$$RH + OH \longrightarrow R + H_2O \text{ ——— (j)}$$

The oxygen atoms may react also to give O_3.

$$O + O_2 + M \longrightarrow O_3 + M \text{ ——— (k)}$$

and the excited molecules may be deactivated or react with hydrocarbon.

$$O_2^* + O_2 \longrightarrow O_2 + O_2 \text{ ——— (l)}$$

$$O_2^* + RH \longrightarrow R + HO_2 \text{ or } RO + OH \text{ ——— (m)}$$

Radical yields are usually below unity for mercury photosensitized decompositions. The formation of peroxides and hydroperoxides are according to the reactions

$$RO_2 + HO_2 \longrightarrow ROOH + O_2 \text{ ——— (n)}$$

$$RO_2 + RO_2 \longrightarrow ROOR + O_2 \text{ ——— (o)}$$

Similarly, formation of alcohol can be attributed to either of the two reactions

$$RO + RH \longrightarrow ROH + R \text{ ——— (p)}$$

$$RO + HO_2 \longrightarrow ROH + O_2 \text{ ——— (q)}$$

According to them, the system is complicated and quenching cross section measurements do not enable a solution to be obtained.

In a subsequent paper, Turner, Callear and Cvetanovic(209) have also favoured reaction (n) to explain their results on the oxidation of ethyl radicals produced by mercury photosensitized hydrogenation of ethylene.

Heicklen and co-workers have studied the mercury photosensitized oxidation of perfluoro-olefins(57 - 63, 205) with molecular oxygen. They say that in the presence of O_2 a number of reactions can occur. O_2 can react with the electronically excited molecule to yield oxidation products.

$$\text{Hg } 6\ ^3P_1 + P \longrightarrow \text{Hg } 6\ ^1S_o + P_o^* \ (469.7 \text{ K J}) \text{ —— (a)}$$

$$O_2 + P_o^* \longrightarrow PO_2 \longrightarrow \text{Products}$$

Oxygen can itself quench the excited mercury atom and

$$\text{Hg } 6\ ^3P_1 + O_2 \longrightarrow \text{Hg } 6\ ^1S_o + O_2^*$$

then may react with perfluoro-olefins to ultimately yield oxidation products. According to their studies, the evidence suggests that the initial step is the energy transfer

$$O_2^* + P \longrightarrow O_2 + P_m^* \ (435 \text{ K J mol}^{-1}) \text{ —— (b)}$$

where P_m^* is a molecule with less vibrational energy than P_o^* (469.7 K J mol^{-1}) formed in the above reaction (a). The mercury photosensitized oxidation of C_3F_6 was examined by Heicklen and co-workers.(205) The products of the reaction were CF_2O, CF_3CFO and smaller amounts of C_3F_6O. The results at high temperatures were the same as those at room temperatures for $\left[C_3F_6\right] \geq 6$ torr and $\left[O_2\right] < 10$ torr. However, at higher $\left[O_2\right]$, the quantum yields of oxidation products became very large at 213°. A long chain was indicated, but the results were quite complicated and were not fully understood. Following mechanism was proposed to explain some of their results:

$$PO_2 \longrightarrow .RO_2^{\cdot} + R: \qquad (1)$$

$$\longrightarrow CF_3CFO + CF_2O \qquad (2)$$

$$\longrightarrow C_3F_6O + O \qquad (3)$$

$$PO_2 + P \longrightarrow 2C_3F_6O \qquad (4)$$

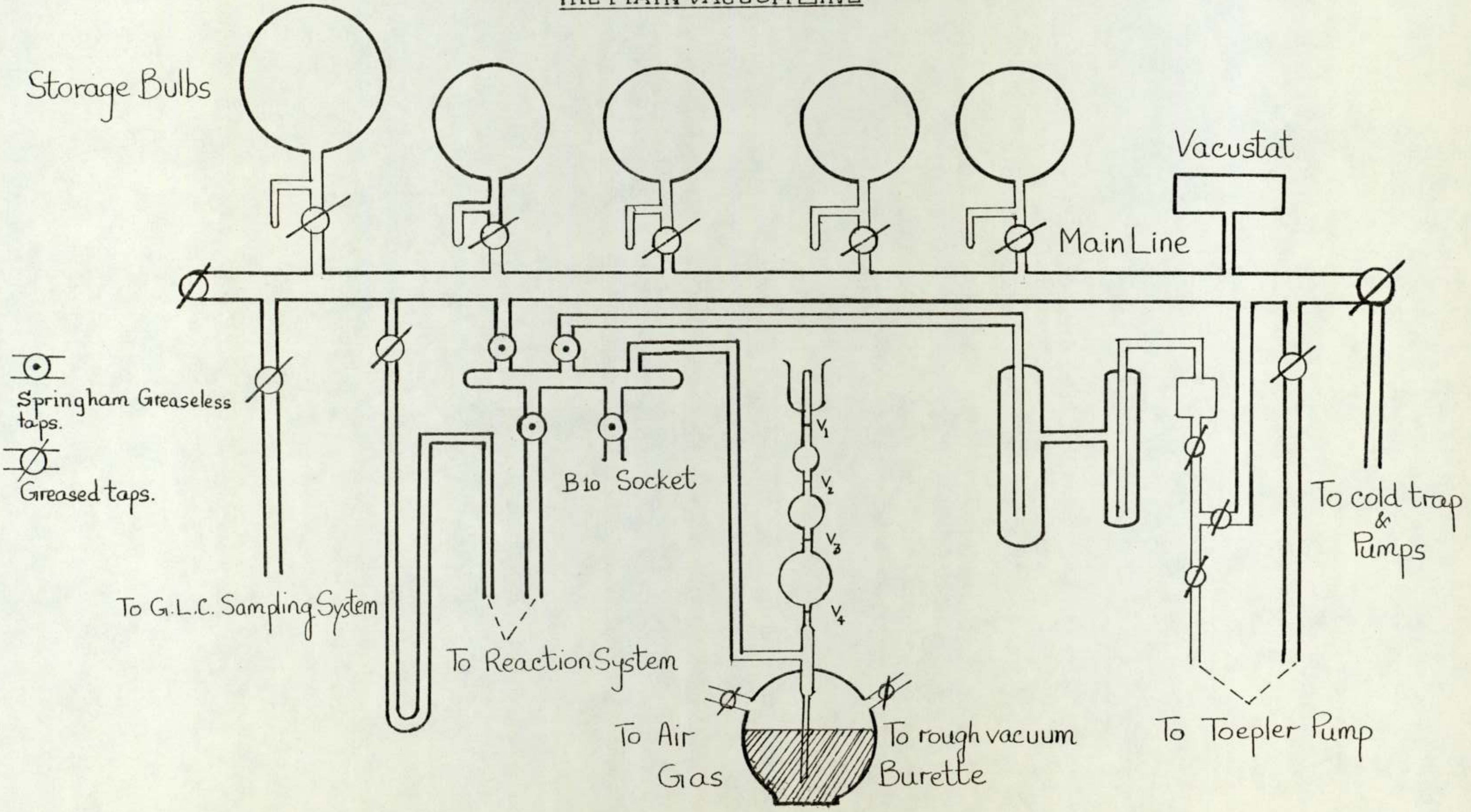
where R is either CF_2 or CF_3CF. They say that reaction (1) was not important in their system but the other three reactions were needed to explain the results.

Due to the complications involved in the system, mercury photosensitized oxidations involving molecular oxygen and olefins have received little attention. Most of the work in this respect has been in a way to use molecular oxygen (in the presence of other reactants such as O^3P atoms) as a radical scavanger. Thus Cvetanovic(53) in his early study of the reaction of oxygen atoms (generated by mercury photosensitized decomposition of N_2O) with ethylene added small amounts of molecular oxygen ($\sim$ 2 mm) in the system. He found that under those conditions very little direct quenching by oxygen occurred. He said that the relatively small increase in ethylene consumption, the independance of the rates on the amount of ethylene, and the suppression of saturated hydrocarbons, suggests strongly that the primary reaction of oxygen atoms with ethylene is not affected by the presence of molecular oxygen, and that the pronounced change in the overall course of the reaction is due to the interaction of oxygen with free radicals formed in the primary process. The same trend is followed in the later experiments with higher alkenes. There was no or very little inhibition of the formation of the addition products, even when the partial pressure of molecular oxygen was relatively high (~ 40 mm). The yields of aldehydes appeared to be slightly lowered and small amounts of new products were also formed. No attempt was made to study in detail these products.

Similarly, Moss and Jennings(65) in their studies on the reaction of oxygen atom with 2-trifluoromethylpropene are in agreement with Cvetanovic that the addition of molecular oxygen did not have any significant effect on the yield of major addition products. They have said that in sensitized system containing only alkene and oxygen, other processes must be considered. Commenting on the basic similarity of the products obtained in their study with molecular oxygen or with oxygen atoms produced by the decomposition of N_2O, they have suggested that the oxygen atoms are involved in Hg^*/O_2 + alkene reaction but nevertheless the possible reactions of excited oxygen and alkene molecules together with the likely presence of ozone in the system made speculation on the reaction processes unfruitful.

In view of the lack of information regarding the mercury photosensitized oxidations of alkenes with molecular oxygen in the gas phase, it was thought that there is a good reason to study in this line so as to acquire a more knowledge and further insight towards the nature of product formation in these reactions in the light of the controversies existing at present.

Fig. 2.1.b
THE MAIN VACUUM LINE



CHAPTER 2

EXPERIMENTAL

2.1. GAS HANDLING SYSTEM

The main apparatus used during this work consisted of a pyrex glass vacuum line built on a metal frame which was mounted on a trolley fitted with wheels. Details of its various components are described below. Experiments done with $^1\Delta g\ O_2$ were performed separately with a microwave discharge system which will be described later on.

2.1.(a). Pumping System:-

The pumping system for evacuation consisted of an Edwards Rotary pump and a mercury diffusion pump which was water cooled. During the process of evacuation pressures of better than 10^{-5} mm. mercury were possible with both pumps working. Pressures better than 10^{-3}mm. were possible with only the rotary pump being working, this being indicated by an Edwards Vacustat. A by-pass was connected to the diffusion pump so that the large amounts of gases not condensible in the main line cold trap should be pumped out without passing through it. Cold trap was surrounded by a dewar of liquid nitrogen (-196^{0}C) when the apparatus was being used.

2.1.(b). Mainline and the Greaseless Manifold:-

The basic features of the mainline are shown in the figure (2.1.b). It was isolated from the pumping system and the cold trap by means of a greased tap, jencons HV10. Gas storage bulbs are attached to the mainline and are isolated from it by means of greased taps. One of these bulbs was of 5 litres capacity and the other four were of 2 litres capacities. Each bulb was having a 'cold finger' so as to condense the gases into them by placing a dewar full of liquid nitrogen around it. Mainline was connected to a mercury manometer by means of a greased tap, usually open all the time. The other limb of the manometer was connected to the reaction system. Volume of the mainline was 600 ml. The other end of the mainline was closed through a greased lid.

The greaseless manifold was connected to the mainline and other sections of the apparatus and was isolated by means of Springham's greaseless taps having fitted with viton A diaphragms. Thus manifold enabled the gases to be transferred from one section of the apparatus to the other, especially from the gas burette to the reaction system without coming into contact with vacuum grease. An inlet-outlet point with a B_{10} socket was also the part of the manifold being attached to it by a greaseless tap.

2.1.(c). Gas burette:-

Gas burette enabled the transference of small amounts of gases at an accurately known pressure to the reaction system. The all four bulbs of different volumes were accurately calibrated. Nitrous oxide being used as the calibrating gas in this case. The different volumes were found to be

$$V_1 = 3.95 \text{ ml.}$$

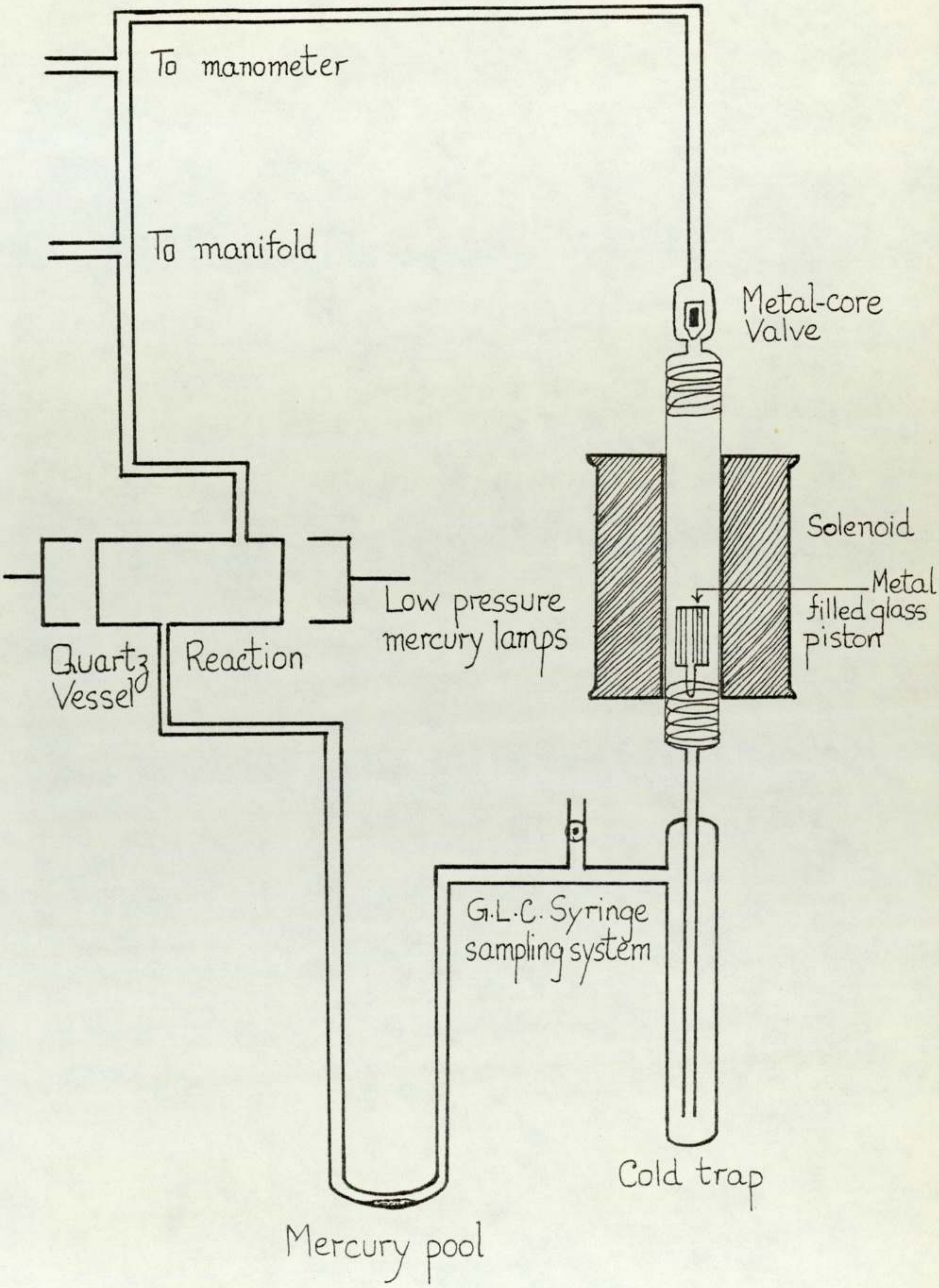
$$V_2 = 18.26$$

$$V_3 = 70.54$$

$$V_4 = 241.99$$

The pressure of gas in any of the bulbs could be determined accurately by measuring the mercury height in the left hand side

FIG. 2.1.(d)



REACTION SYSTEM

limb when the level was coincided with the graduation mark provided for the appropriate bulb. Zero reading could be determined during the evacuation. The mercury level in the bulbs could be monitored by means of the two side taps in the mercury reservoir. One of the two was attached to a rough pump while the other was open to the atmosphere by a narrow tubing. Gases were transferred into the burette by means of freezing them in the smallest bulb (cold finger) at the top of the burette putting liquid nitrogen in the reservoir surrounding the finger.

2.1.(d). Reaction System:-

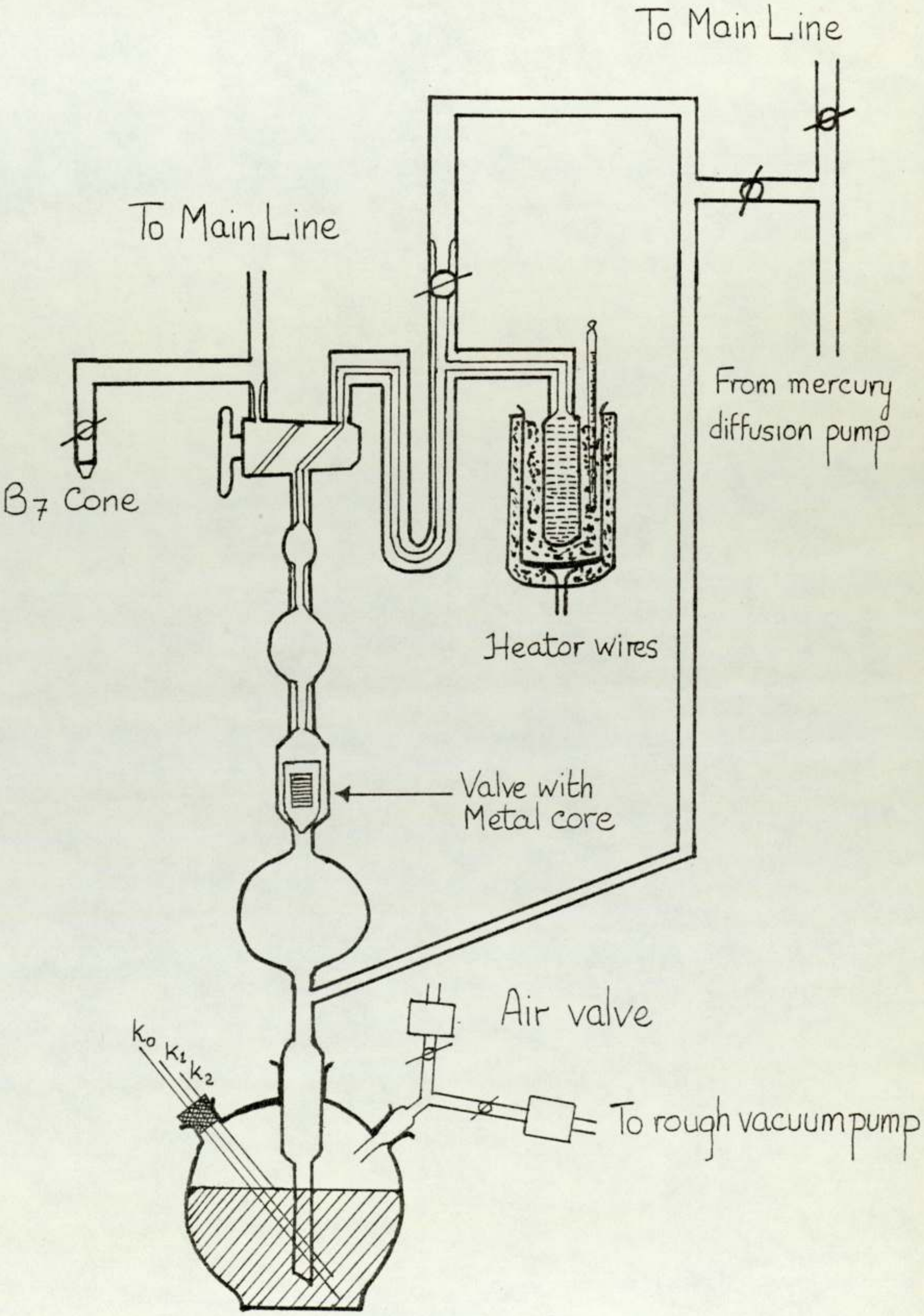
The greaseless reaction system as shown in the figure 2.1.(d) consisted of a circulating pump, a quartz cell, a shallow pool of mercury to ensure that the reaction mixture remains saturated with mercury vapour at room temperatures and a cold trap to enable the transfer of gases from other parts of the apparatus. Reaction mixtures could be freezed in the cold trap after the irradiation and it also allowed the removal of non-condensibles to the toepler pump. It was connected to the mainline, analysis line and the G.L.C. sampling system via greaseless taps through the manifold. All the pressures in the reaction system were measured by a mercury manometer which was attached via a greased tap. The volume of the reaction system was 760 ml.

The reaction cell was a cylindrical vessel ten cms. long and 5 cm. in diameter and made up of quartz. It was connected to pyrex glass at both inlet and outlet. Irradiation of 253.7 n.m. was provided by means of two Hanovia (type 752/68) low pressure mercury lamps. The power to the lamps was provided by the mains via a constant voltage 15 watt transformer to ensure a steady output. The lamps were fitted inside cylindrical cans which acted both as a support for the quartz spiral and as a beam collimator during the process of irradiation. Both the lamps were placed at about nine cms from the opposite ends of the quartz reaction cell. The arrangement of two lamps was used to achieve more uniform light intensity and hence uniformity in the reaction throughout the whole cell and not just near the cell windows.

The all glass circulating pump is shown in the figure (2.1.d.). It was constructed such that all the surfaces exposed to the reactant gas were pyrex glass except for the springs which were coated with Telcothene. These springs were changed and new springs made up of polymeric material were used. These reduced the noise to a minimum and there was little or no heating problem involved. The piston was a sealed pyrex glass tube containing a number of mild steel rods held rigidly inside the glass envelope with "Telcothene". It was enclosed within another close fitting tube. There was enough clearance so as to enable the piston to move freely. The springs were cushioned between the piston and the extremes of the outer glass casing.

The coil was mounted on a brassformer and consisted of approximately 5,000 turns of lacquered 22 gauge wire of total resistance 40 Ω . By means of connecting the power to the small electric motor, a cam was driven. It was shaped in such a way that it made contact with a microswitch opened and closed once every second.

FIG. 2.1. e



TOEPLER PUMP & CuO FURNACE

A metal cored valve at the top of the circulating pump ensured a unidirectional flow of gas within the system. During the evacuation of the system, it could be held upwards with a permanent horseshoe magnet. By the operation of the circulatory pump thus a possibility of secondary reactions of the primary products are kept to a minimum.

2.1.(e). The Gas Analysis System:-

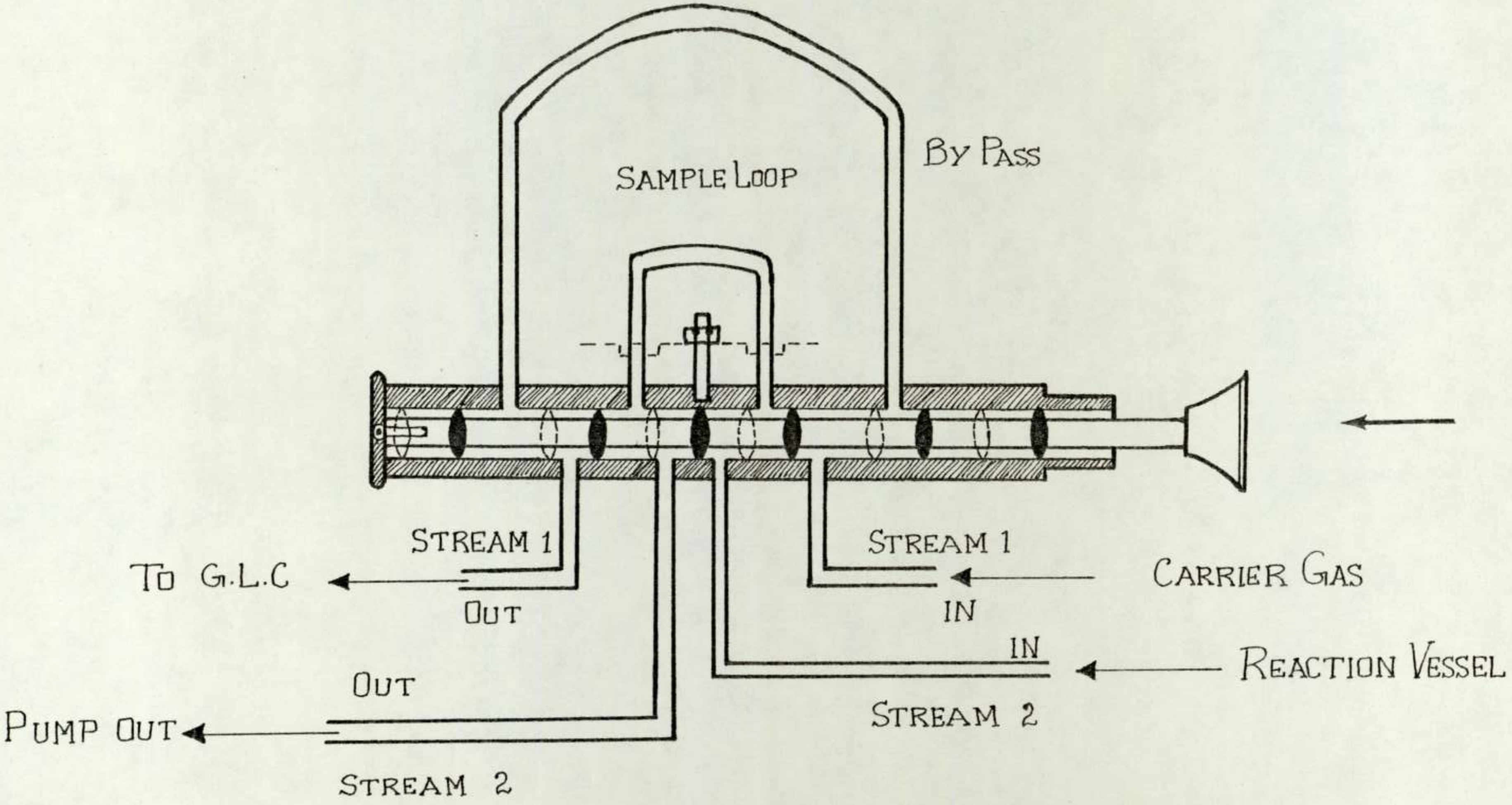
The analysis system is comprised of two fixed cold traps connected with an automatic Toepler pump with a gas burette. It was connected and can be isolated from the mainline via the manifold through a Springham's greaseless tap. Another mercury diffusion pump was used for the transfer of gases (usually non-condensibles) from the reaction system to the gas burette. The purpose of the two cold traps with dewars of liquid nitrogen around them is to prevent any condensible gases from reaching on to the Toepler gas burette. After a reaction was performed the non-condensible products were collected and measured in toepler pump gas burette. The sample could be retained in the toepler gas burette by a ground glass valve with a metal core sealed by a pool of mercury. Manipulation of the valve was possible by means of a permanent magnet. The operation of raising and lowering the mercury to trap the gas above the toepler pump valve was automated. Three platinum contacts were inserted in the mercury reservoir for this purpose, as shown in the figure (2.1.e.). The air inlet and rough vacuum valves were controlled by electromagnetic valves. When the mercury level was risen in the burette, it pushed the valve upwards, thus making it possible for the trapped sample to be collected and measured in one of the fixed volumes of the burette. During the lowering of mercury, the valve blocks the thin outlet, thus always retaining a small pool of mercury within which prevents the trapped sample from escaping back. When the toepler pump power was not to be used then the raising and lowering of mercury level could easily be controlled manually.

The copper oxide furnace was connected to the top of the toepler pump gas burette through a three way greased tap. The non-condensible gases which were trapped above the valve could either be removed away through an outlet having a B_{10} socket or they could be passed on to the copper oxide furnace as shown in the figure. The furnace was made up of a pyrex tube packed from inside through thin copper wires. A cold trap in the shape of a U-tube was situated between the furnace and the three way greased tap. Any carbon monoxide in the non-condensible gases could be estimated by transferring the gases to the furnace having a temperature of $240^{0}C$. Gases are usually kept there for an hour, after which they were cooled in the trap and retoeplered to the gas burette. Any carbon monoxide in the mixture is oxidised to carbon dioxide which condenses at 77^{0} and hence is not recovered.

Calibration of the toepler pump gas burette was performed as follows:

A measured amount of gas is taken from the already calibrated gas burette and is transformed to the volumes v_1 and v_2 of the toepler pump gas burette by means of the toepler pumping system. Pressures were noted from a mirror scale placed behind

FIG. 2.1.(f)



GAS SAMPLING VALVE

the straight limb of the burette for this purpose. The volumes after the calibration were found to be

$$V_1 = 3.14 \pm 0.01 \text{ ml.}$$

$$V_2 = 11.91 \pm 0.01 \text{ ml.}$$

2.1.(f). Gas Sampling Valve:-

A greaseless sampling valve was used throughout this work for the injection of sample onto the column of the gas liquid chromatography. The valve used was made by H.C. Engineers Ltd. and was of type GSV-106-S.

The advantage of using such a valve is that the sample could be injected directly from the reaction system onto the column of the G.L.C. Evacuation of the valve was possible by means of a greased tap which connected and isolated it from the main line. The valve also contains a 10 ml. sample loop attached on the top of it. Sample is transformed into the loop after the evacuation while the valve itself is isolated from the mainline, it is then injected into G.L.C. as shown in the figure (2.1.f.). When the metal knob is in out position, the valve can be connected to the mainline via the greased tap, but is usually isolated from the reaction system, but when the knob is in IN position, then it is connected with the sampling system through a greaseless tap whereas it is isolated from the mainline.

Large samples (up to two or three atmospheres) can be successfully injected into the G.L.C. by first condensing them in the sample loop and then, after warming up, introducing into the G.L.C. Usually this is required during the separation and collection of products.

During the analysis, when a sample is taken from the reaction system, pressure is reduced and hence the corresponding peak areas also drop down for the next sample. It was necessary therefore to introduce sampling correction factors. It was calculated in terms of the reaction system volume and the sample volume. The sampling correction factor for the first sample was given by the relation

$$\frac{\text{R.S volume} + \text{S.volume}}{\text{R.S. volume}}$$

All the peak areas were hence corrected for the sampling error by multiplying the actual area measured by the corresponding sampling correction factor. The correction factors for successive samples are given below. This reduced the error in peak areas to better than ± 2%.

TABLE 2.1.f.

Sample No.	Correction Factor	Sample No.	Correction Factor
1	1.0278	5	1.1469
2	1.0563	6	1.1788
3	1.0857	7	1.2116
4	1.1159	8	1.2452

2.2. GAS LIQUID CHROMATOGRAPHIC EQUIPMENT

The whole equipment consisted of a Perkin Elmer F11 gas chromatograph equipped with a flame ionization detector (F.I.D.) and a Kent recorder type 66/52501/11 equipped with a disc chart integrator for the measurement of peak areas (143 counts per sq.cm.). The carrier gas used during the work was nitrogen but helium gas was used during the collection and the purification of the products and different materials. A flow control unit provided the controlling of flow rate of the nitrogen gas while hydrogen (28 lbs./Sq.in.) and air (30 lbs./Sq.in.) supply was controlled by the pressure control unit. A constant supply of hydrogen and air for the flame throughout the experiments was important.

Two columns were tried for this work. Porapak Q and 20% dinbutylpthalate columns. Porapak Q of 4 m. and 3 metres were tried at different temperatures by making use of a linear temperature programmer. The programme being operated usually 5 minutes at initial temperature (about $30^{\circ}C$) and then heated up to a final (150, $\xrightarrow{200}$, 250) temperature at $18^{\circ}C$ per min. It was noted that the separation was not good and reproduceable after doing many runs. A 4 metres 20% di-n-butylphthalate column was found to be generally successful for these experiments, for a temperature range of room temperature to $35^{\circ}C$. Separation and collection of products during all the studies were also done on this column at room temperature.

Detector and the amplifier were part of the F-11 equipment used. Output from the detector was fed into the ionisation amplifier and the output from this was fed into a Kent recorder (1 millivolt input).

The working of a flame ionization detector is usually as follows. When a sample is injected onto the column of G.L.C., the carrier gas takes it along and feeds to a flame of high purity hydrogen burning in air. Organic components present are burnt, and decomposition to highly unsaturated intermediates occurs, which finally broke down to carbon. This is ionized and the charged particles along with the electrons from the decomposition are collected by the electrodes in an electric field applied to the flame. The current thus formed is amplified, converted into a voltage and fed into the recorder. A flame ionization detector usually allows accurate product analysis at low conversions. To calculate the absolute value of the amount of a particular product formed, the detector must be calibrated in the following way.

2.2.(a). Calibration of the Detector:-

The calibration was done by taking the known amount of a pure sample of the product in one of the fixed volumes of the gas burette. It is then transferred to the reaction system and nitrous oxide approximately 600 m.m. of Hg was added. It was thoroughly mixed and circulated for about 40 minutes. Samples were then injected onto the column of the G.L.C. After taking three successive readings, half of the reaction mixture was removed away. Again it is thoroughly circulated and three further readings are taken to obtain a reproducible chromatogram. Calibration factor of the flame ionization detector can then be calculated from the relation.

$$P = f.A$$

where P is the pressure of the sample,

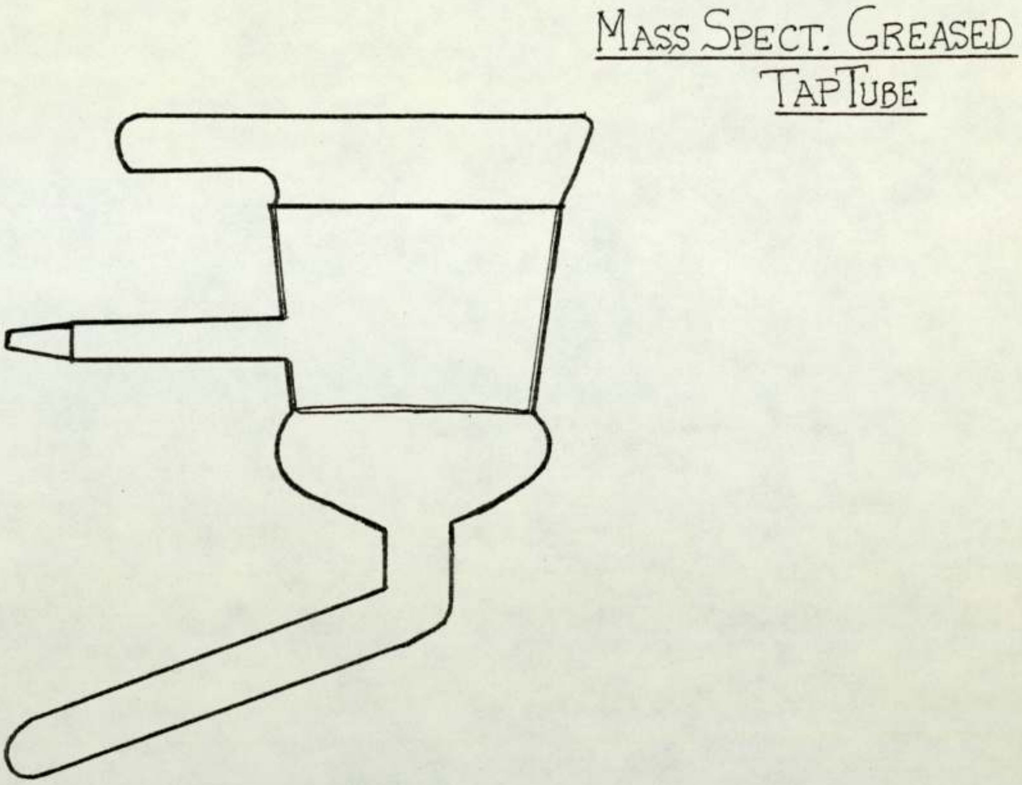


FIG. 2·3·(a)

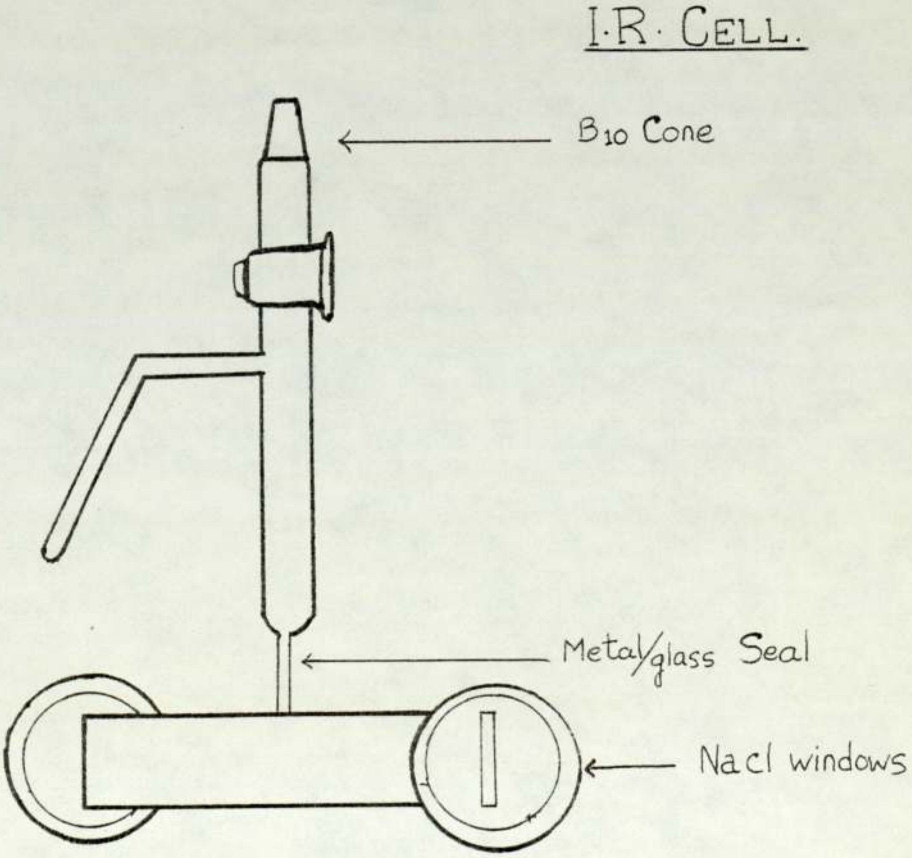


FIG. 2·3·(b)

A is the peak area of chromatogram,

and f is the calibration factor of the detector.

2.3. THE AUXILIARY EQUIPMENT

(a) Mass Spectrometer:-

By means of special greased tap tubes, samples for the mass spectrometric analysis could be transferred directly from the apparatus through the B_{10} outlet of the manifold (Fig. 2.3.a.). The sample was put through a Varian leak valve in place of the normal solid sample probe on the mass spectrometer. In the present study, two spectrometers were used for the purpose, an A.E.I. M.S.9 spectrometer (up to 50,000 M) and the Micromass 6, which can record masses up to 100 M.

(b) The Infra-red Equipment:-

The infra-red spectrometer used for the identification of products and other purposes was the Perkin-Elmer 237 type. Spectra were normally run from 4,000 cm^{-1} to 600 cm^{-1} using a reference beam attenuator and a gas microcell. Gases were introduced into the miniature cell through a B_{10} socket attached with a mini greased tap which was joined to the cell by means of a metal to glass seal (see fig. 2.3.b.). The total volume of the cell was approximately 7.7 ml. The cell itself consisted of a piece of rectangular brass tubing and had sodium chloride windows at both ends. A cold finger was attached to the cell so that the small amounts of gases could be condensed into it. It was necessary to have pressures of between 30 and 100 m.m. Hg to obtain a good spectra.

2.4. EXPERIMENTAL PROCEDURES

2.4.(a). Oxidation Runs with Molecular Oxygen:-

The mercury diffusion pump being on and a dewar of liquid nitrogen placed under the main line cold trap, the whole system was evacuated for at least thirty minutes so as to obtain a pressure better than 10^{-4} m.m.Hg. The valve at the top of the circulating pump was held open using a permanent magnet (also during the degassing process). Mercury was then let to rise in the gas burette up to the top. The required amount of olefin was then introduced in the mainline and the approximate measure of the pressure was noted down, (absolute amount is measured in the gas burette). It is then condensed into the reaction system through the manifold via a greaseless tap by means of keeping a dewar of liquid nitrogen around the reaction system cold trap. It is then degassed twice by opening the system to the pumps. Main line and manifold are again isolated from rest of the system and oxygen is introduced directly from the cylinder into the mainline through the outlet of the manifold. Its pressure being noted down, it is also transferred into the reaction system. Since it does not condense in liquid nitrogen, hence during high pressure runs the pressure of oxygen in the mainline and the manifold should be kept at a maximum in order to transfer large amounts of it into the reaction system. Usually it requires two or three introductions of oxygen from the cylinder into the mainline during the high pressure runs. Reaction system is then isolated from the rest of the system and the reaction mixture is allowed to warm up and circulate for about forty minutes or so, so as to obtain an equilibrium to room temperature and a complete mixing. With the shutters still being on the lamps are switched on at this stage to warm up before the irradiation starts. Usually the lamps are switched on 15 minutes before irradiation. Before the irradiation starts, the total pressure in the reaction system is noted down along with the room temperature. Shutters are then removed and the irradiation starts for the required time. After the irradiation is complete, the lamps are switched off so is the circulating pump. Room temperature is noted again and the introduction of samples into the G.L.C. begins through the sampling valve.

2.4.(b). Run with Nitrous Oxide:-

During a run with nitrous oxide after the amount of olefin has been transferred into the reaction system, the known amount of nitrous oxide is expanded in the mainline from the storage bulb. After noting down the pressure, it is also condensed in the reaction system. The reaction system is then degassed by opening it to the pumps. The reaction mixture is then allowed to warm up during which the reaction system is isolated from the mainline and the pumping system. It is again degassed and then allowed to warm up for a period of forty minutes prior to the irradiation. After this, the rest of the procedure is same as described above in 2.4.(a)., except that when the irradiation stops and the sample is ready for G.L.C. analysis, then before the analysis measurement of non-condensibles are made, to calculate the amount of nitrogen formed. This can be described as follows.

2.4.(c). Measurement of Non-Condensible Gases:-

The reaction mixture was frozen down after the irradiation in the reaction system cold trap and the circulating pump valve was kept open by means of the permanent magnet. It was kept frozen for about ten minutes. Dewars of liquid nitrogen were then placed beneath the two analysis system cold traps and then the analysis system was open to the reaction system while both being isolated from the mainline. The toepler mercury diffusion pump aided the transference of the non-condensibles from the reaction system into the analysis system. The metal core valve in the toepler pump gas burette was released by removing the magnet and the toepler pump was started to operate for at least fifteen minutes. (The toepler diffusion pump and the copper oxide furnace both are started an hour before the measurement to commence). At this stage, the reaction mixture is warmed up and again frozen. After ten minutes the collection of non-condensibles was repeated in the same manner as described above. The pressure and temperature of the gases trapped above the toepler pump valve were measured, till a constant reading is obtained.

The non-condensibles trapped above the toepler gas burette were now transferred to the copper oxide furnace which was having a temperature of 250°C. A U-tube situated in between the furnace and the gas burette was immersed in the liquid nitrogen. It was to trap any carbon dioxide and water formed in the combustion process. The gases were then left for at least an hour in the furnace to ensure the conversion of carbon monoxide into the dioxide. Readings were noted from time to time till a constant value is read. The copper oxide furnace was then open to the toepler gas burette and the toepler pump was again operated for fifteen minutes. This was done to collect the residual nitrogen back in the toepler gas burette. When there was no pressure change in the gas burette, then the pressure of nitrogen in one of the fixed volumes V_1 and V_2 was noted along with the temperature. This was then used to calculate the amount of nitrogen formed during a run.

While the measurement of non-condensibles was in progress, the reaction mixture was allowed to warm up and circulate for at least 40 minutes. The sampling system was open to the pumping system. When the evacuation was complete, having a pressure of better than 10^{-3} in the Vacustat, then a sample was injected directly onto the column of G.L.C. from the greaseless sampling valve. Three such samples were injected to have reproducible chromatograms.

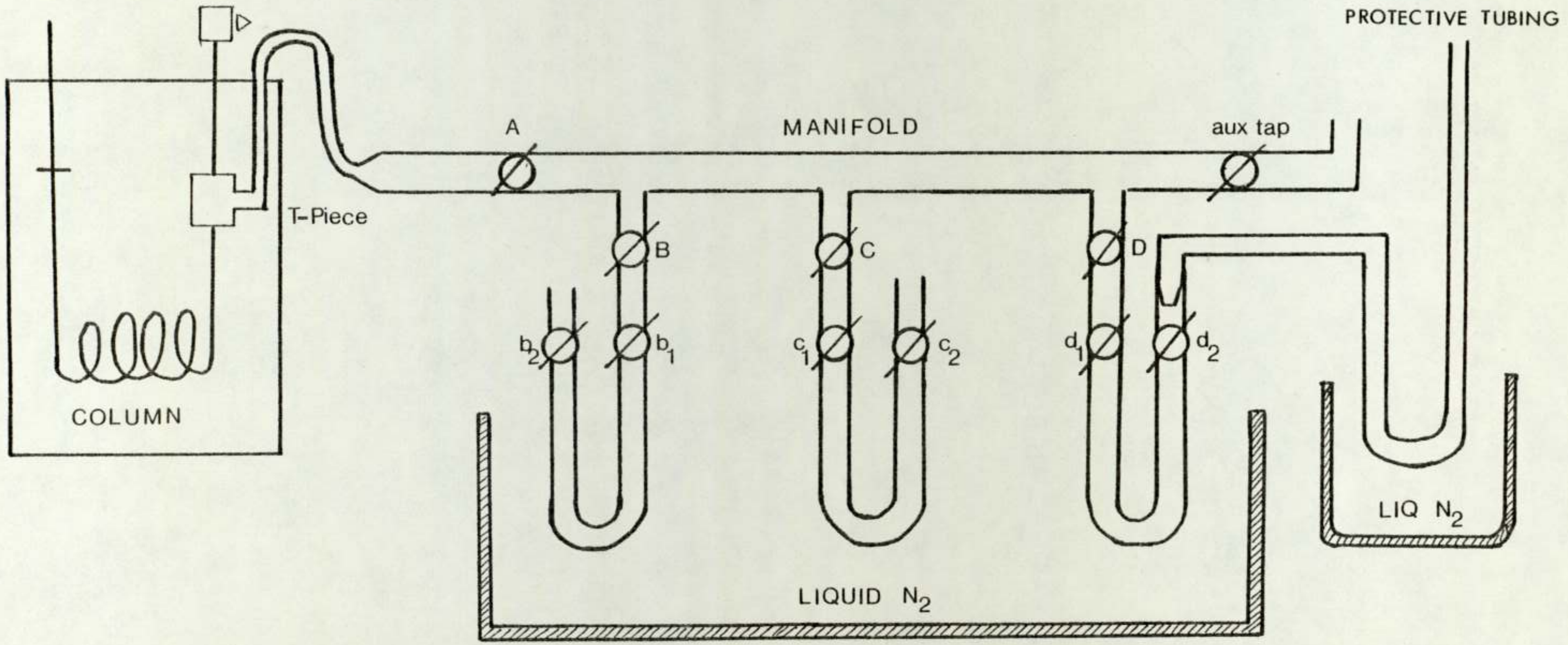
2.5. COLLECTION AND IDENTIFICATION OF PRODUCTS

For collection of products, very long irradiation times were needed in order to have larger quantities. It was found that with molecular oxygen, very low conversions were taking place when compared with nitrous oxide experiments during the same irradiation periods. It was necessary to have the irradiation times as high as five times to that of nitrous oxide. The reaction mixtures were irradiated for at least twenty-five hours in the present study so as to have enough amount of products formed for collection. The whole process took place as follows:

The reaction mixture was irradiated for twenty-five hours usually taking three days. It was usually frozen down during the rest period when irradiation was not taking place. A sample was then fed onto the G.L.C. so as to ensure that a sufficient amount of products has been formed, and also to verify the positions of the product peaks on the chromatogram. The reaction mixture was then frozen down in the reaction system cold trap using liquid nitrogen. All the unreacted oxygen which is not condensible at the liquid nitrogen temperatures was pumped away. When all of it was removed, leaving the reaction mixture fully saturated with the products, then about 100 m.m. of nitrous oxide is added. By keeping the reaction system isolated, the reaction mixture is allowed to warm up and circulated for at least 30 minutes.

Helium was used as a carrier gas at this stage because by using nitrogen the collection tubes which are kept at liquid

FIG. 2·5



TRAP SYSTEM FOR COLLECTION OF PRODUCTS

nitrogen temperatures will start condensing it and would soon be blocked. A chromatogram is again taken.

The products were collected using a trap system connected directly to the Gas-liquid chromatography as shown in the figure (2.5.). A T-piece was inserted between the column and the flame detector, and was connected to the manifold of the product isolation equipment. The arrangement was such that when the tap A was opened the sample injected could be diverted into the manifold instead of passing onto the flame detector. The manifold had three openings through greased taps B, C and D to each of which three collection tubes (U-tubes with a tap at each limb) could be attached for the collection of three products simultaneously. Auxiliary tap is used to let any uninterested product escape into the atmosphere. Since liquid nitrogen was used as a coolant, hence a protective tube was always connected to the free limb of the collection tube in order to prevent back diffusion of air. The products separated were condensed in the U-bend of the collection tubes as they eluded.

As large samples were needed during the collection of products (2-3 atmospheric pressure) hence a small amount of cotton wool dipped in liquid nitrogen was placed inside the 10 ml. sample loop so as to condense a larger sample. It was then warmed up by a dryer and then injected onto the G.L.C. column.

When the products in the form of peaks start appearing on the chromatogram, then when the peak of interest starts to elude the gas stream is diverted into the manifold by opening the microtap A. It is then condensed in the collection tube by first opening the tap attached to the protective tube and then opening the tap attached to the manifold, in order to stop the flame being faded off e.g. as shown in the fig. 2.5., first open b_2, c_2 or d_2 and then B, C or D. The taps b_1, c_1 and d_1 remain open and are closed when no more sample is required . The flame must be on during the collection.

After the collection is complete, the U-tubes are attached to the mainline of the vacuum system through auxiliary greaseless tap still immersed in liquid nitrogen to be degassed. The product was then carefully measured in one of the fixed volumes of the gas burette and was then transferred to either the I.R. cell for infra red spectroscopy or to the mass spectrometric tube for the mass spectrometric analysis.

An alternative technique which was found very useful for preliminary identification of products is described as follows:

After a usual experimental run with the alkene a chromatogram was taken and the position and size of the peaks were noted. Keeping in mind the retention times of the different products on the column being used, a particular product was tried for identification by means of mixing a small quantity of its pure sample with the reaction mixture which changes the nature of the peak on the chromatogram. This was usually done as follows. A very small quantity (< 1 m.m.) of the pure sample of a suspected peak is introduced in the gas burette through the auxiliary greaseless tap. It is degassed twice and then transferred to the reaction system. The whole reaction mixture is warmed up and mixed thoroughly. A sample was then introduced onto the

G.L.C. column and the nature and the position of the peaks are matched with the previous chromatogram taken before the introduction of the known sample. If the peak, which is suspected to be the same as the known sample introduced increases quite markedly, then it is assumed to be the same. In this way, a number of pure samples of various known compounds suspected to be present as products, in the reaction mixture, can be mixed with it and the peak positions and sizes are matched with the normal chromatograms. If there is no change in the peak size but a new peak is observed in the chromatogram, then it is fair to assume that the compound introduced is not amongst the products formed and hence is excluded.

Although this technique suffers from some disadvantages, such as the samples of substances in the liquid state having low vapour pressure are difficult to transfer to the reaction system and that it can be useful only when the compounds under study are easily obtainable, but nevertheless it can be of some value during the preliminary identification of products.

In the present study, this alternative technique was found to be very useful, especially during the identification of the minor products, since their very small quantities formed made them impossible to collect for an I.R. and mass spectrometry analysis. Almost every product was identified in this way and were later on confirmed by using other techniques as well (I.R. and mass spectrometry).

2.6. MATERIALS AND THEIR PURIFICATION

The materials used during this study were obtained commercially and some of them necessitated purification as described below:

(a) Nitrous Oxide:-

This was obtained from British Oxygen Company. It was degassed twice and then purified over the activated charcoal, the procedure being as follows.

A small cold trap with a B_{10} attachment containing activated charcoal in it was attached to the main line through the inlet/outlet point on the manifold (auxiliary tap in fig. 2.1.(b)). Trap was gently heated under vacuum to activate the charcoal till the pressure in the line was better than 10^{-3} mm. Hg. The gas to be purified was first degassed twice in the storage bulb and then was allowed to expand in the mainline. It was then condensed onto the charcoal and left for about ten minutes, during which it was open to the pumping system for thorough evacuation. The gas was then allowed to warm up during which the first few millimeters were rejected through the pumping system. Only the middle fraction of the gas is collected, while the rest of it is rejected by isolating the cold trap from the mainline. The purified gas collected was then transferred back to one of the storage bulbs by condensing it in the cold finger of the storage bulb. It was later on checked on the G.L.C. for any impurities present and was then ready for usage.

(b) Oxygen:-

This was obtained from the British Oxygen Company and was usually transferred directly from the cylinder to the reaction system without any further purification.

(c) Propene:-

This was obtained from B.D.H. and was 99% pure. This was used after degassing twice.

(d) Ethylene:-

This was obtained from Cambrian Chemicals and was purified over activated charcoal.

(e) Butene-1:-

This was obtained from B.D.H. and was 99% pure. It was used after purification over heated charcoal.

(f) 2-Methyl Propene:-

This was obtained from B.D.H. and was 99% pure. This was further purified over activated charcoal and was used after degassing twice.

(g) Cis and Trans Butene-2:-

Both of these were obtained from B.D.H. and were 99% pure. They were used after degassing twice.

(h) Acrolein:-

This was of Cambrian Chemicals Ltd. and was used after degassing twice.

(i) Methacrolein:-

This was of Ralph N. Emanuel Ltd. and was used after degassing twice.

(j) Ammonium thio cyanate (Koch Light Labs.) and Ferrous sulphate AR (Fisons) were used without purification. Similarly the rest of the chemicals, including Tert. butyl hydroperoxide (Koch Light Labs.), Propionaldehyde AR (Fisons), n-butyraldehyde AR (Fisons), Isobutraldehyde AR (Fisons), Acetone AR (Fisons), and Methyl-

Ethyl Ketone AR (Fisons) were also used after degassing twice only.

(k) Propylene oxide:-

This was obtained from B.D.H. Chemicals and was 99.5% pure. It was used without further purification.

(l) α - Butene Oxide:-

This was prepared in the laboratory by the reaction of oxygen atoms with Butene-1 and then separating the epoxide by the method described in section 2.5. It was used after degassing twice.

(m) Isobutene-oxide:-

This was also prepared by the reaction of oxygen atoms with 2-Methyl propene and then separating the epoxide as explained in section 2.5. This was also used after degassing twice.

CHAPTER THREE

RESULTS OF MERCURY PHOTOSENSITIZED OXIDATION WITH 2-METHYL PROPENE

3.1. INITIAL SURVEY OF MERCURY PHOTOSENSITIZED OXIDATIONS OF C_2 TO C_4 ALKENES

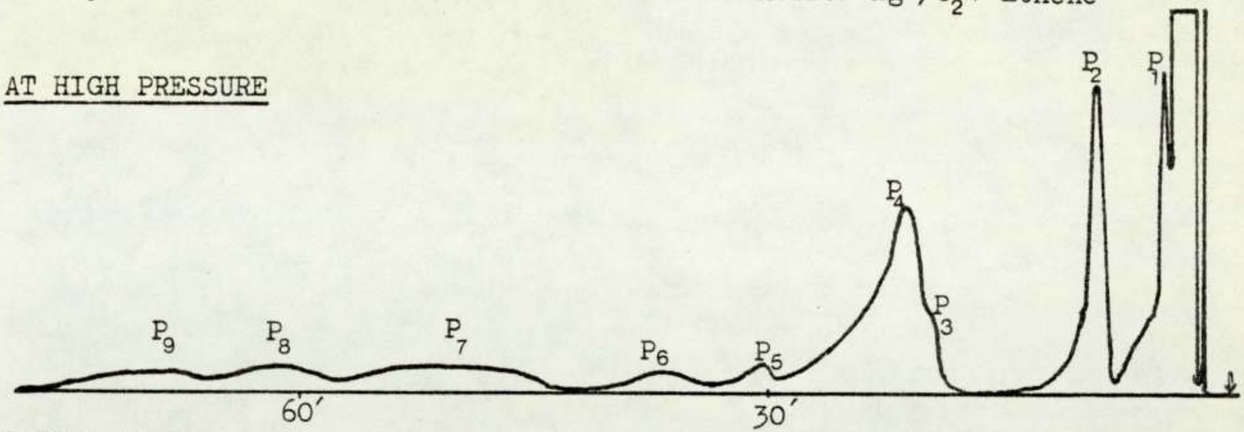
All the experiments were carried out at room temperature and the irradiation time for a typical run was five hours (unless otherwise stated) so as to have a reproducible chromatogram. Before the actual runs were carried out, many experiments were done in order to determine the suitable conditions for the G.L.C. The ratio of oxygen to alkene was kept in excess of (10 : 1). The choice of column was finally laid onto a 4 meter 20% di-n butyl phthalate + 2% Carbowax on which the separation and reproducibility of products was much better. Another column used occasionally was a Porapak Q 4 meters.

After doing a lot of experimentation work using both atomic and molecular oxygen under different conditions, some preliminary investigations were carried out with different individual alkenes. The aim was to obtain general standard conditions for the experimental work and to get the preliminary information regarding the oxidations to be carried on with the individual alkenes.

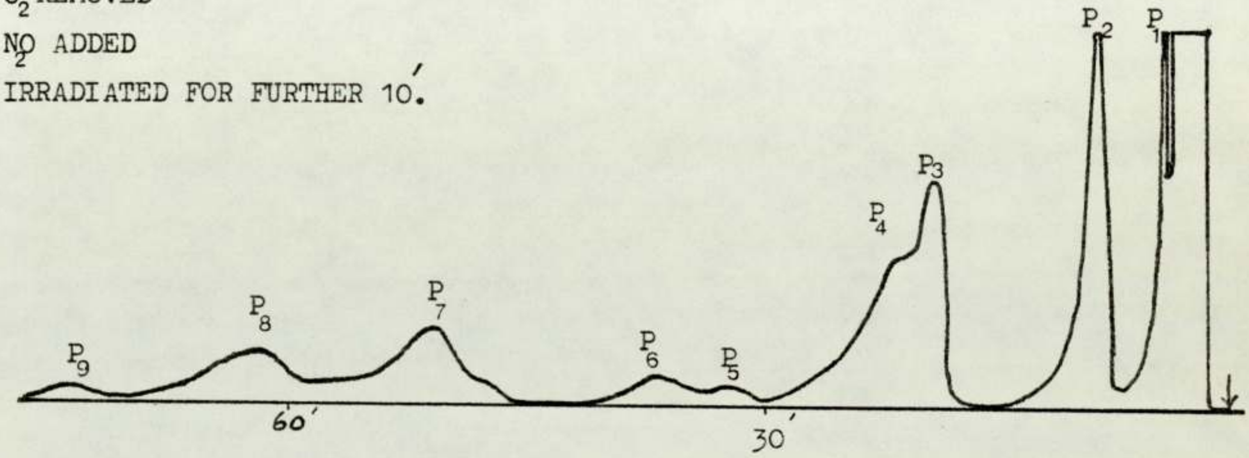
The results of such investigations are provided in the standard chromatograms in figs. 3.1.(a) to 3.1.(f). They were to be used as reference for the G.L.C. operating conditions as well. In a typical run after the 5 hours irradiation time, all the molecular oxygen was pumped away and nitrous oxide was added of the

FIG. 3.1.(a). GAS CHROMATOGRAMS FOR THE REACTION Hg^{*}/O_2 + Ethene

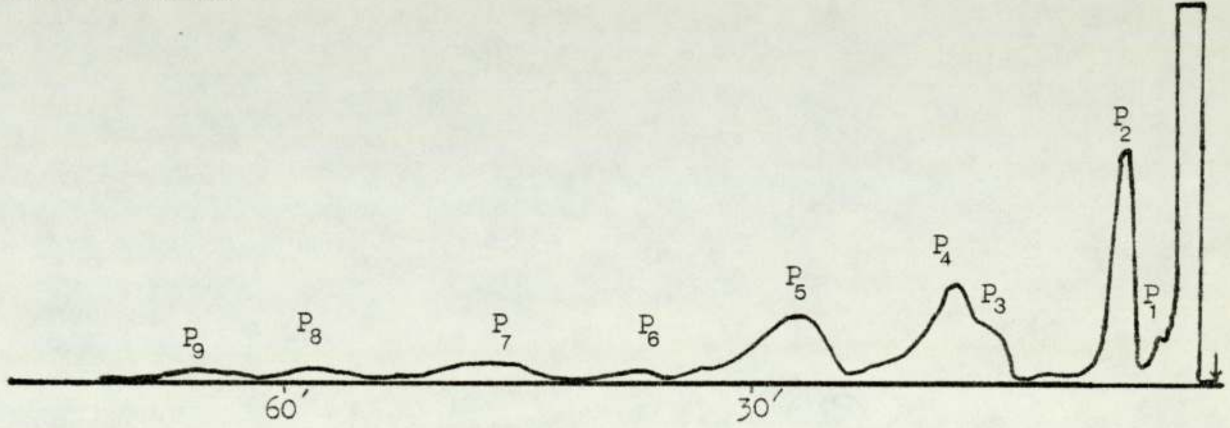
AT HIGH PRESSURE



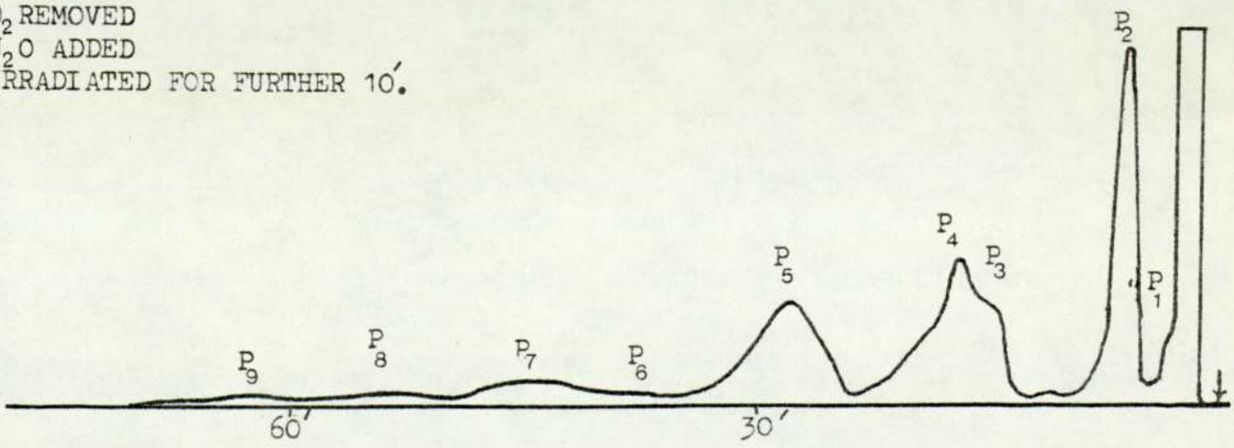
O_2 REMOVED
NO_2 ADDED
IRRADIATED FOR FURTHER 10′.



AT LOW PRESSURE



O_2 REMOVED
N_2O ADDED
IRRADIATED FOR FURTHER 10′.



required pressure. The whole reaction mixture was then mixed and further irradiated for 10'. The object was to make a preliminary identification of those products which arise from oxygen atom reaction.

As can be seen from the chromatograms, these reactions were quite valuable as they provided in general the following observations:

1. The nature of some of the products formed with molecular oxygen (in Hg^*/O_2) seem to be quite similar to those formed by oxygen atoms in (Hg^*/N_2O) reaction.
2. The products which appear to be the same should have a different mechanism for their formation as their yields are very low comparative to the products from O^3P atoms in (Hg^*/N_2O) reaction.
3. It is seen that with one or two exceptions usually the yield of products in the higher pressure runs (700 m.m.) seem to be always less than the lower pressure runs (100 m.m.) keeping the irradiation time similar in both cases.
4. Relative yields seem to be at least 20 - 25 times lower than the corresponding oxygen atom (O^3P) reaction.

In the forthcoming paragraphs, some individual alkenes will be dealt with very briefly and a fair guess is made about the nature of products formed by means of their appearance on the G.L.C. chromatogram.

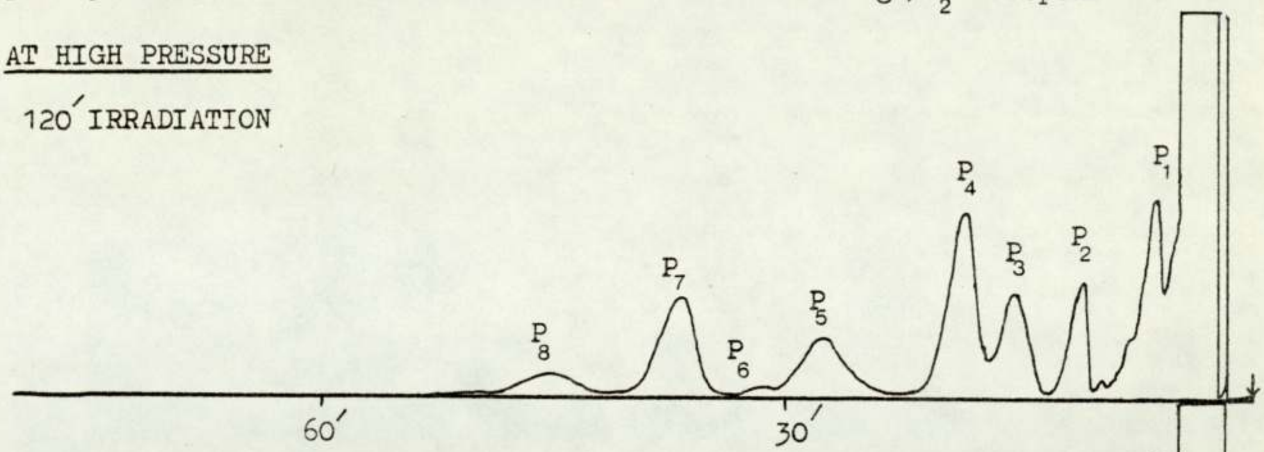
3.1.(a). Ethene

In fig. 3.1.(a), typical chromatograms of the reaction products are shown. It can be seen that in spite of 5 hours irradiation time, the yields are quite low. There seem to be nine

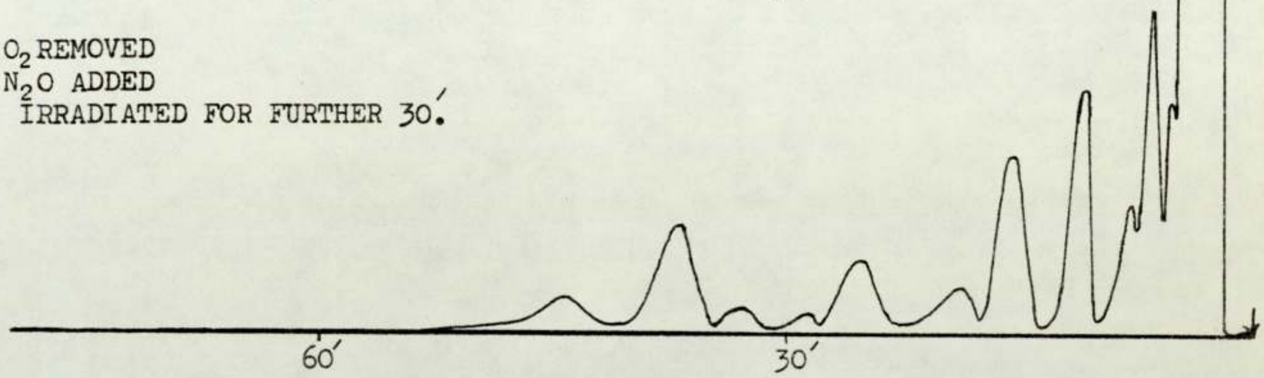
FIG. 3.1.(b). GAS CHROMATOGRAMS FOR THE REACTION Hg*/O_2 + Propene

AT HIGH PRESSURE

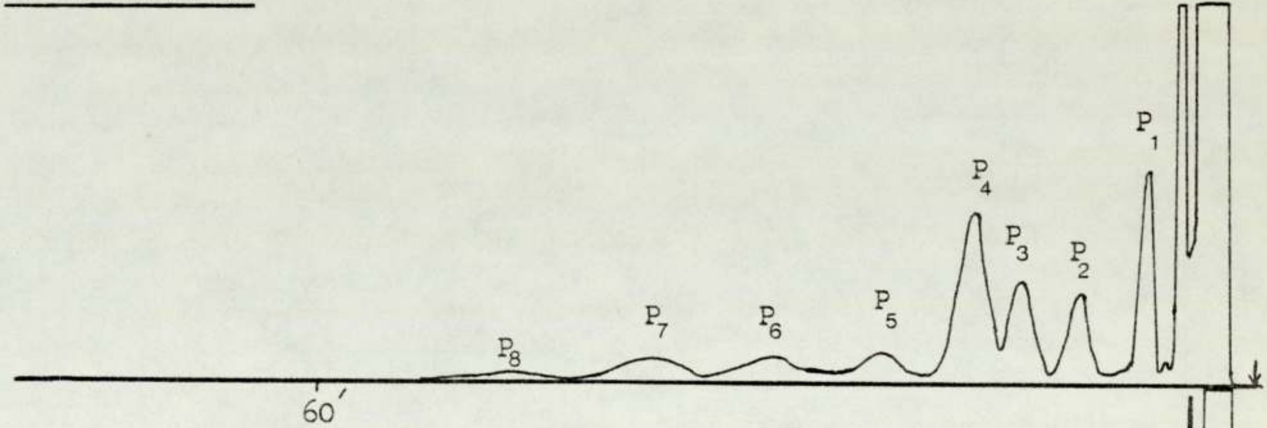
120' IRRADIATION



O_2 REMOVED
N_2O ADDED
IRRADIATED FOR FURTHER 30'.



AT LOW PRESSURE



O_2 REMOVED
N_2O ADDED
IRRADIATED FOR FURTHER 12'.

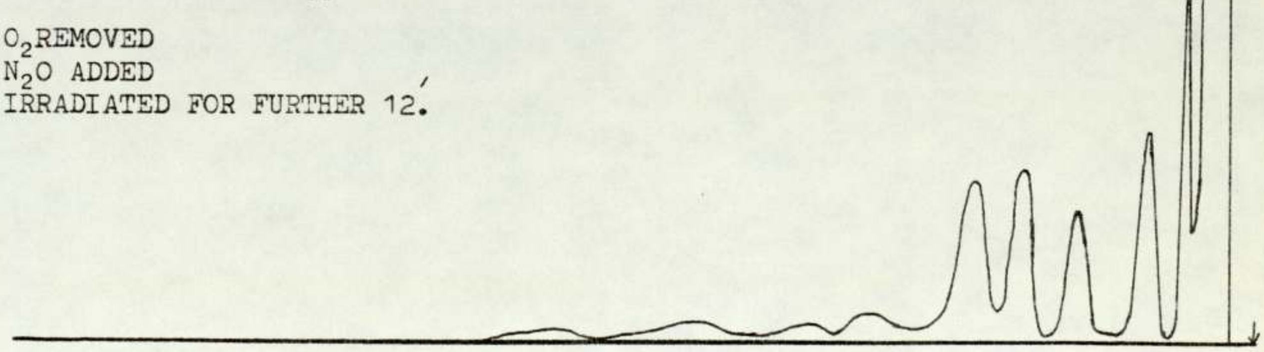
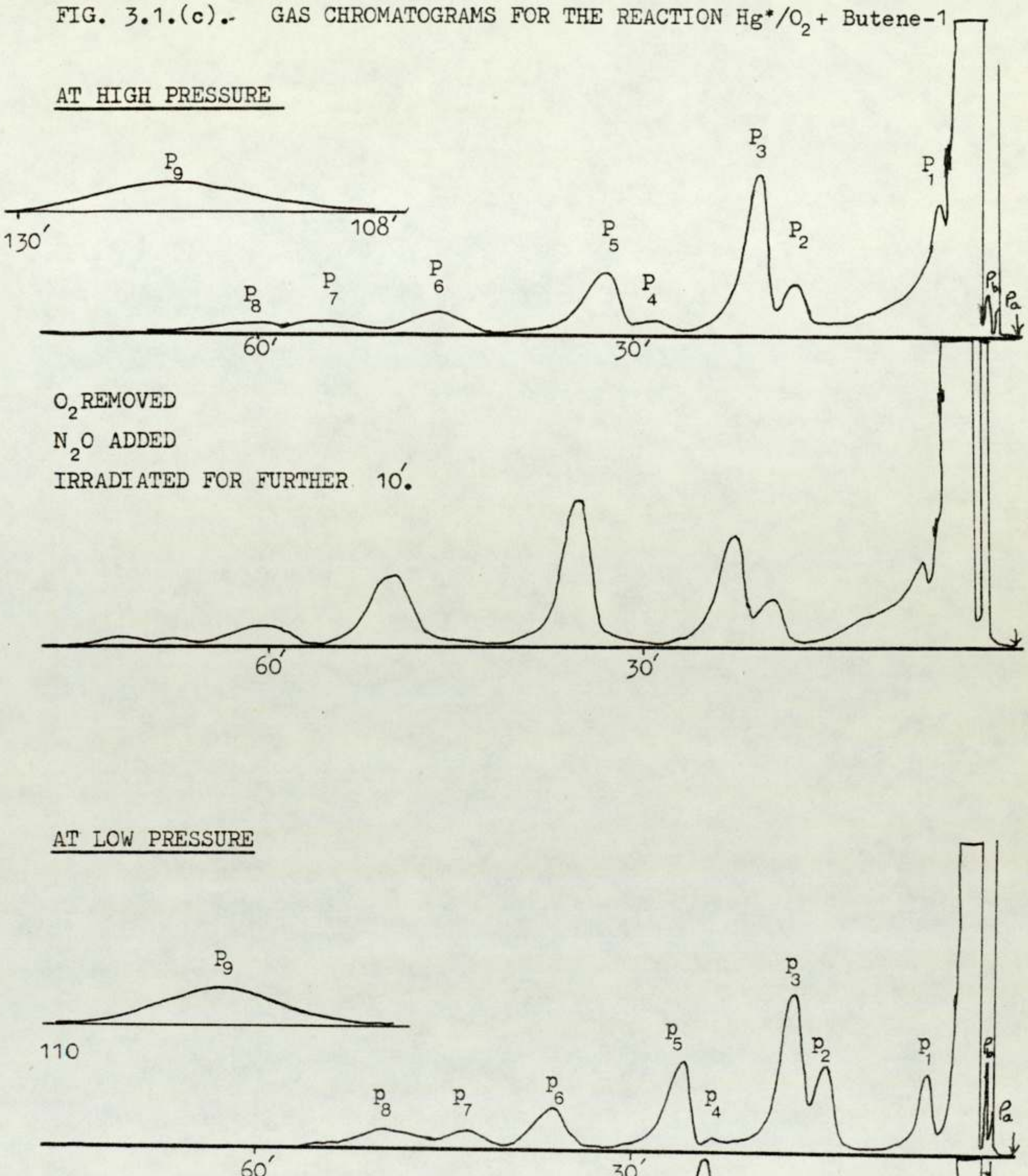


FIG. 3.1.(c).- GAS CHROMATOGRAMS FOR THE REACTION Hg*/O_2 + Butene-1



products arising from the reaction. The yield of product P_4 is large as can be seen from its peak, so is product P_2. The yield of product P_5 increases at lower pressure indicating some pressure dependant fragmentation. The product peaks P_2 and $P_3 + P_4$ increased quite markedly when N_2O was added and the reaction mixture was irradiated for 10'. This was to indicate that they might be the products arising from the reaction of oxygen atoms. Although it is very difficult before the separation and identification to speculate on the type of products formed, but at least one of the products (peak P_2) seems to be acetaldehyde by the nature of its retention time. Nevertheless, the reaction of ethene seems to be quite complex.

3.1.(b). Propene.

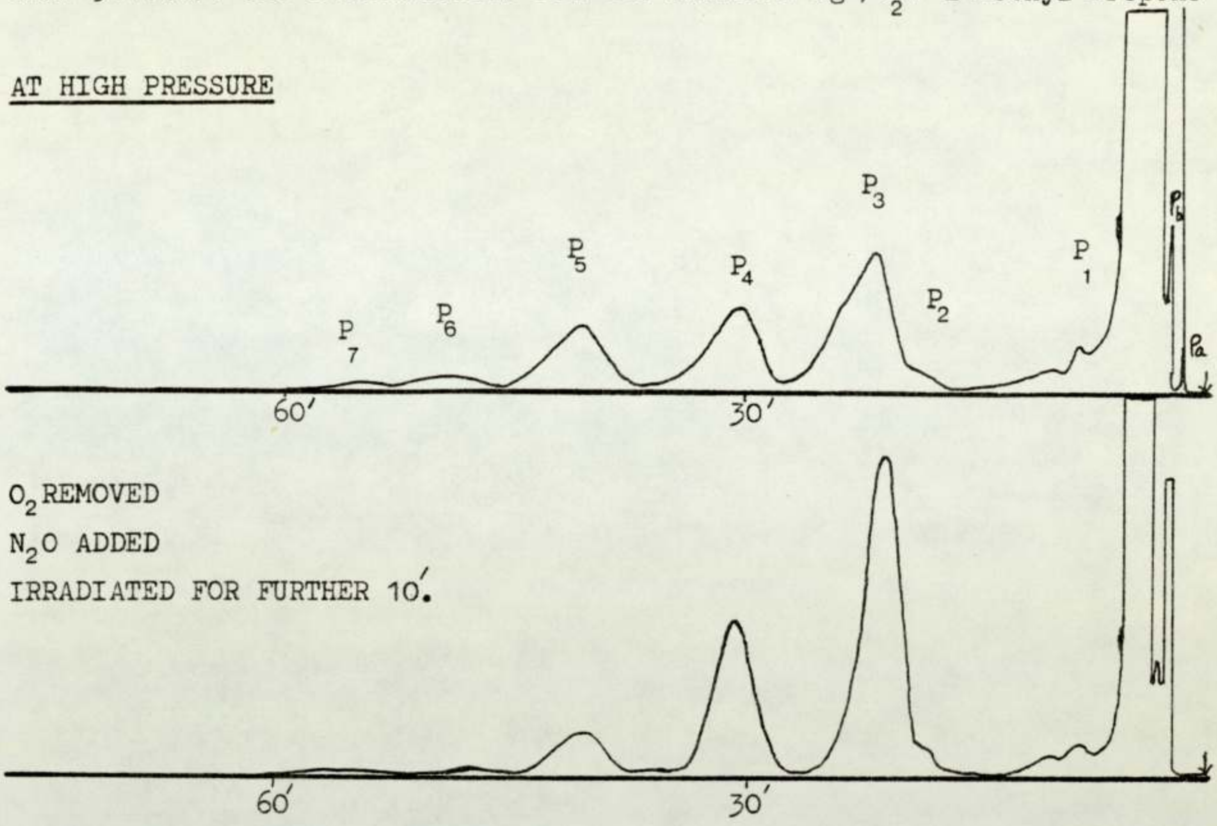
In fig. 3.1.(b). the chromatograms for the reaction is provided. There seem to be eight product peaks. The peak A only appears in the low pressure runs. The first four P_1 - P_4 seem to be major products with P_7 also having significant yield. The irradiation in presence of N_2O does not have much effect on product peak P_4 suggesting it to be a genuine molecular oxygen product. Again, product P_1 seems to be acetaldehyde, whereas products P_2 and P_3 have shown marked increase in presence of N_2O and seem to be arising from oxygen atom reaction. They are thought to be propeylene oxide and propanal.

3.1.(c). Butene-1

The chromatograms for the reaction products are provided in figure 3.1.(c). Apart from the two early eluding products (may be alkane and/or alkene), the reaction yields 9 products. In the presence of N_2O when reaction mixture was irradiated, it can be seen

FIG. 3.1.(d). GAS CHROMATOGRAMS FOR THE REACTION Hg*/O_2 + 2-Methyl Propene

AT HIGH PRESSURE



AT LOW PRESSURE

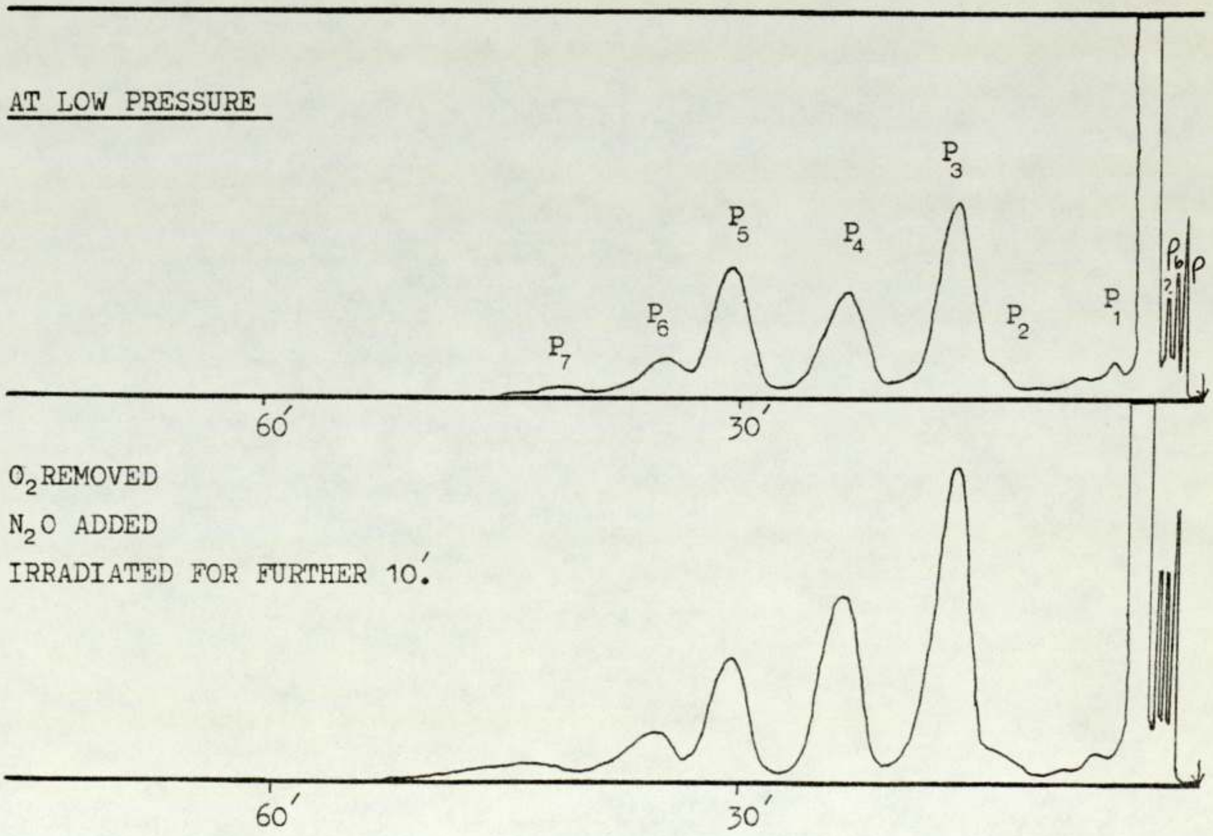
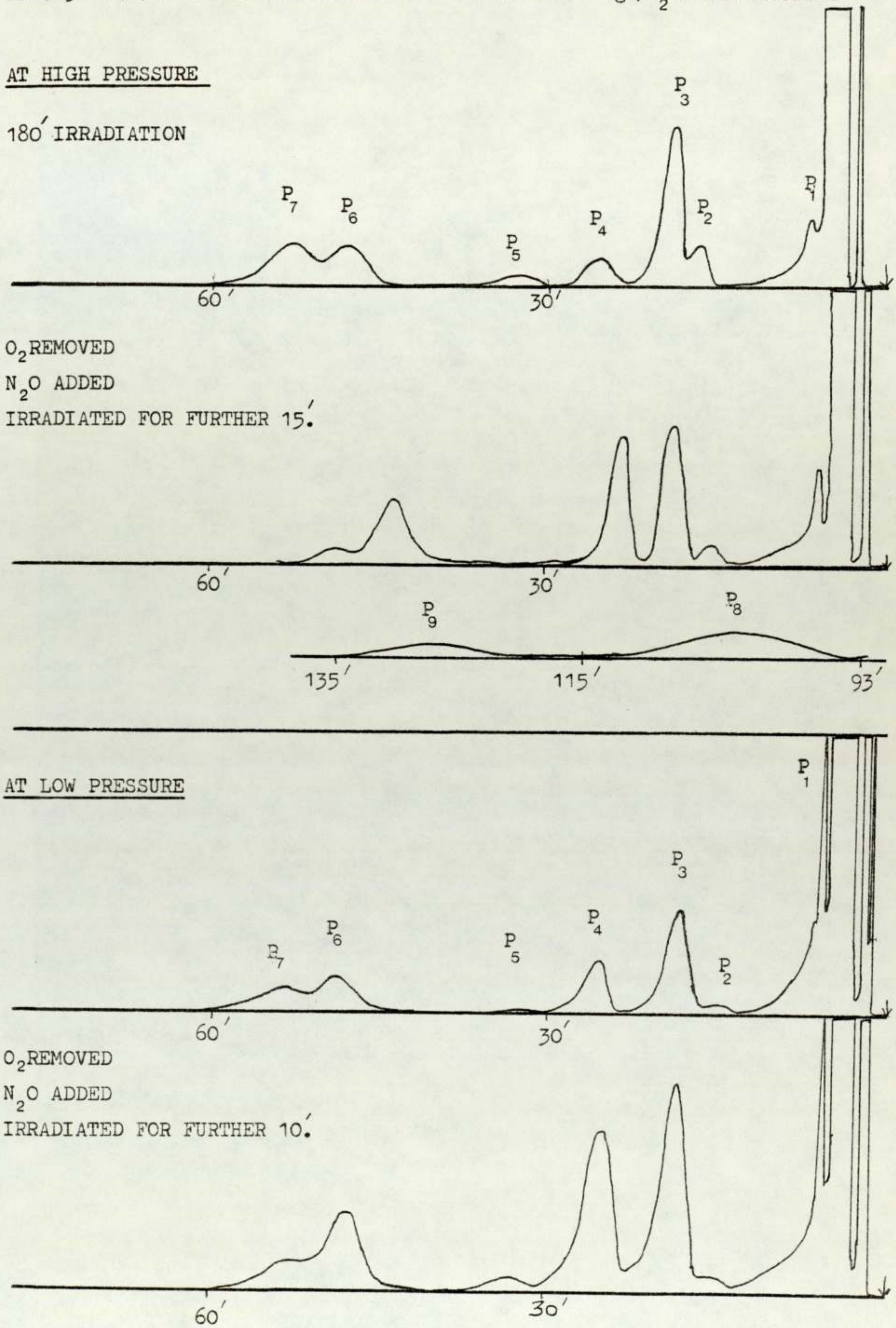


FIG. 3.1.(e). GAS CHROMATOGRAMS FOR THE REACTION Hg^*/O_2 + Cis Butene-2



AT HIGH PRESSURE

180′ IRRADIATION

O_2 REMOVED
N_2O ADDED
IRRADIATED FOR FURTHER 15′.

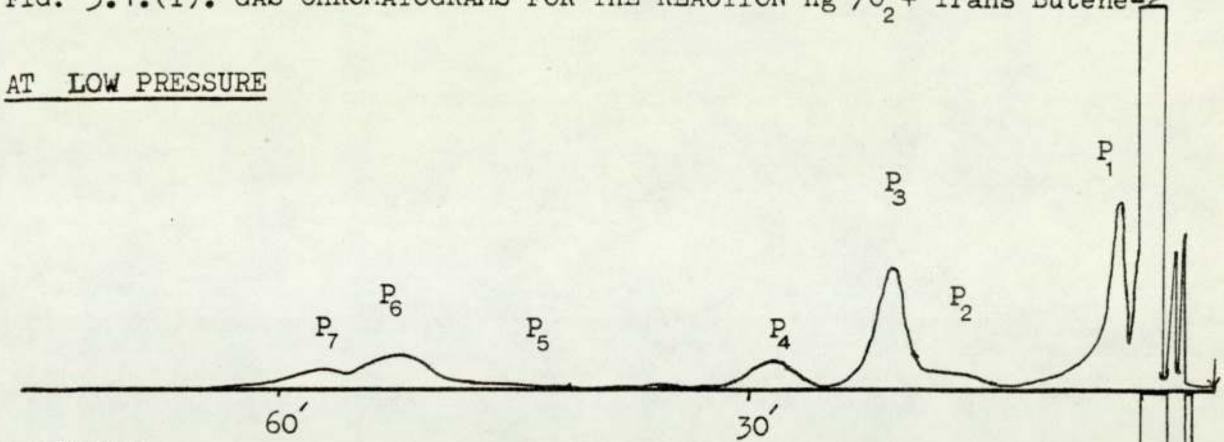
AT LOW PRESSURE

O_2 REMOVED
N_2O ADDED
IRRADIATED FOR FURTHER 10′.

Product peaks P_8 & P_9 were also present in the case of Trans Butene-2

FIG. 3.1.(f). GAS CHROMATOGRAMS FOR THE REACTION Hg^*/O_2 + Trans Butene-2

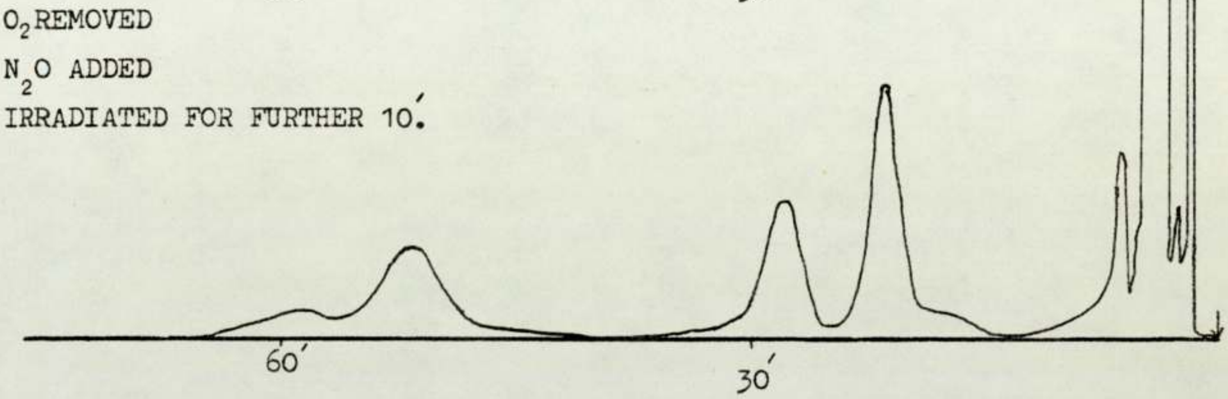
AT LOW PRESSURE



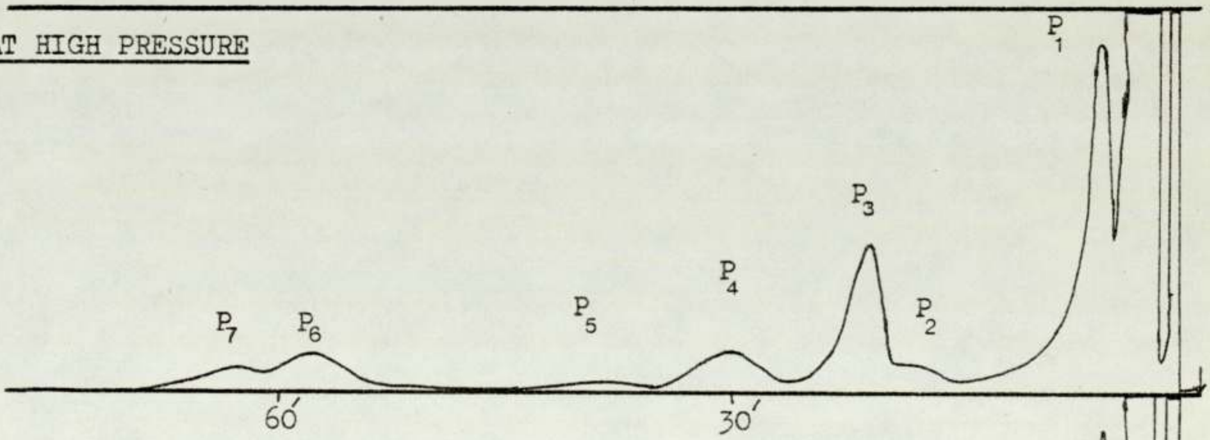
O_2 REMOVED

N_2O ADDED

IRRADIATED FOR FURTHER 10'.



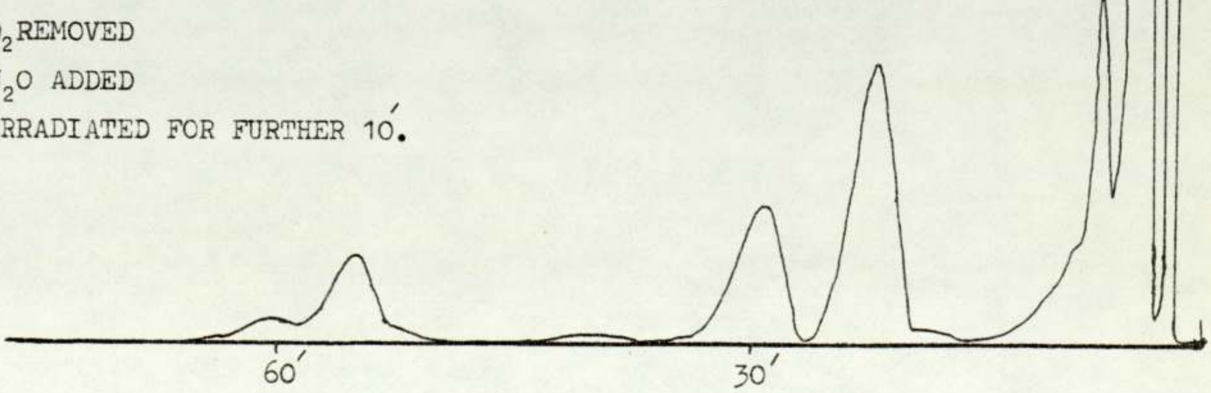
AT HIGH PRESSURE



O_2 REMOVED

N_2O ADDED

IRRADIATED FOR FURTHER 10'.



that product peaks P_5 and P_6 increased quite apparently whereas there was no or very little effect upon the peaks P_2 and P_3, suggesting them to be genuine molecular oxygen products. In fact after the oxidation run P_3 has the larger yield than any other product. By means of the effect of nitrous oxide upon the products P_5 and P_6, it can be assumed that they may be α - butene oxide and n-butraldehyde. P_1 again seems to be acetaldehyde and P_2 and P_3 can be anything among the propionaldehyde, acetone, ethyl alcohol, etc. The elution time of one of the product is very long ~ 90 minutes. Yield of products at low pressure is higher.

3.1.(d). 2-Methyl propene

The results of the chromatograms for 2-methyl propene are provided in figure 3.1.(d). Like butene-1 there are two early peaks and apart from them the total reaction products seem to be seven. Product peaks P_2 and P_3 seem to overlap and product peak P_5 seems to tail off with P_6. The irradiation in presence of N_2O results in the increment of peaks P_3 and P_4, suggesting them to be the epoxide and aldehyde respectively. Product P_5 seems to be genuine molecular oxygen product, as its yield was not affected by N_2O. The yields are better at low pressure.

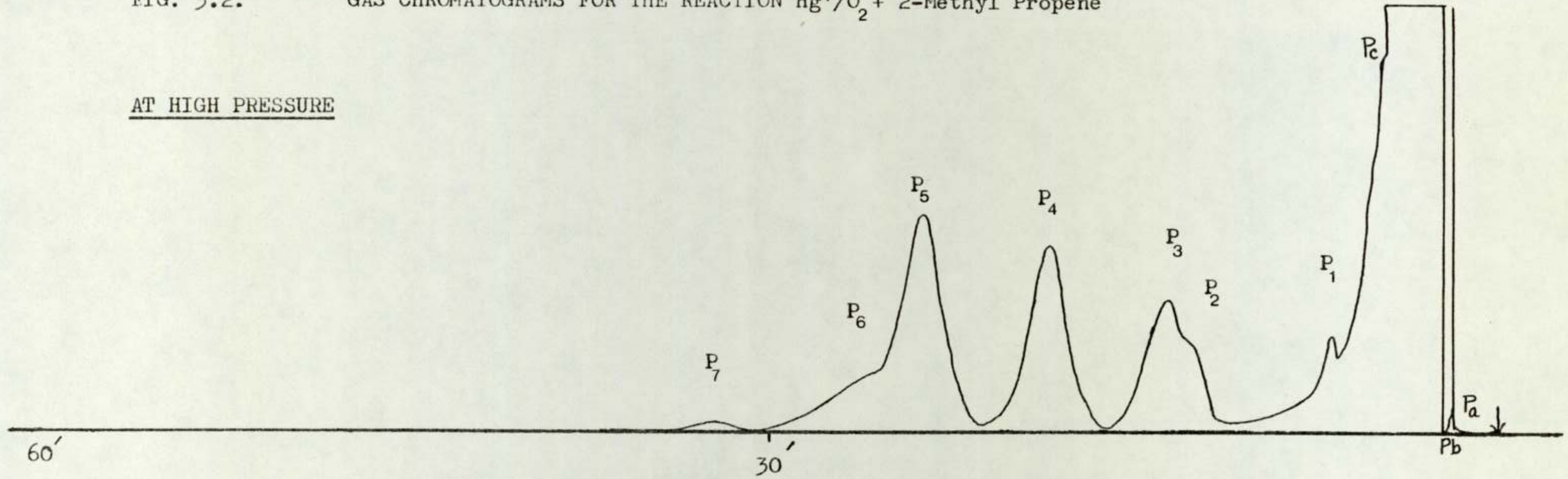
3.1.(e). Cis-Butene-2 and Trans Butene-2

The chromatograms for both alkenes are provided in figures 3.1.(e) and 3.1.(f). Apart from two early eluding peaks, the total reaction products amount to nine in each case. The chromatogram seem to be alike with little differences. Product peaks P_3, P_4 and P_6 increase upon the irradiation in presence of N_2O, suggesting them to be epoxides and aldehyde.

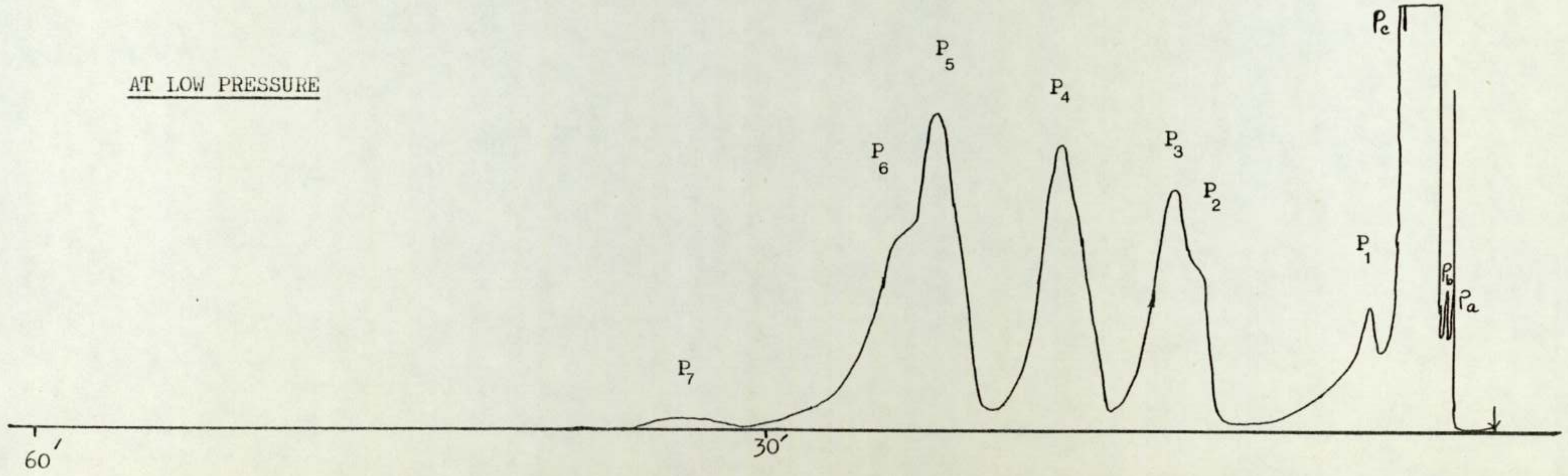
After carrying out the initial oxidations, it seemed that there were some similarities in the nature of products when compared with the oxygen atom reactions. At this stage, it was thought necessary to carry out a detailed product separation and identifications of some of the individual alkenes, so that a detailed study can be made and various points could be cleared. Propene and 2-Methyl-propene were selected for this purpose. The remainder of this chapter will be concerned with the detailed results of 2-methyl-propene.

FIG. 3.2. GAS CHROMATOGRAMS FOR THE REACTION Hg^{*}/O_2 + 2-Methyl Propene

AT HIGH PRESSURE



AT LOW PRESSURE



3.2. CHROMATOGRAMS FOR 2-METHYL PROPENE

A typical chromatogram at both high and low pressure for the reaction of 2-methyl propene with Hg^*/O_2 is presented in fig. 3.2. Irradiation time during a normal standard run was five hours. All studies were made at room temperature. Column used throughout the reaction study was a 4 meter di-n butylphthalate with 2% Carbowax kept at 35 ± 2°C. Gas pressures for the G.L.C. were

$$P_{N_2} \text{ (carrier gas)} \longrightarrow 30 \text{ lbs./in.}^2$$

$$P_{H_2} \longrightarrow 28 \text{ lbs./in.}^2$$

$$P_{Air} \longrightarrow 30 \text{ lbs./in.}^2$$

The symbols used in the chromatograms for the products are explained below.

'P_1'	represents	the	product	Acetaldehyde.
'P_2'	"	"	"	Propanal.
'P_3'	"	"	"	Acetone.
'P_4'	"	"	"	2-Methyl Propanal.
'P_5'	"	"	"	Methacrylaldehyde.
'P_6'	"	"	"	Tertiary Butanol.
'P_7'	"	"	"	2-Butanone.

P_a, P_b and P_c represent unidentified products. They correspond to less than 2 % of the main products at high pressure ~ 700 m.m. At low pressures about ~ 100 m m. these products were found to be less than about 4 %.

3.3. IDENTIFICATION AND ANALYSIS OF PRODUCTS

As explained in the preceeding chapter 2, by using different methods of analysis, the products identified are listed in Table 3.3. The different techniques used for the identification are also summarized.

The products confirmed by using Mass spect. and I.R. techniques were the major products, which were isolated by G.L.C. from high conversion runs. The minor products, due to low yields, could not be isolated and hence were confirmed by other alternative techniques as were possible.

Brief notes are provided below for each of the individual compounds.

1. Acetaldehyde.

Acetaldehyde was a minor product and its quantity formed during the high conversion runs was too small for collection and separation. It was identified by the retention times on only one column, di-n butylphthalate. Also after the addition of a small amount of a known pure sample of acetaldehyde in the reaction mixture and following the method described in section 2.5., when a chromatogram was taken the acetaldehyde peak increased. No further identification was thought to be necessary. It is also a known product of molecular oxygen, its species ozone and oxygen atoms, and alkene systems.

2. Propanal.

The propanal peak occurred just before the acetone peak and due to very small yields even at very long irradiation times, this again could not be collected for identification by I.R. and Mass spect. techniques. However, using the two alternative techniques

TABLE 3.3.

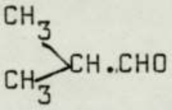
PRODUCTS	IDENTIFICATION METHODS					
	G.L.C. Ret. Times	By Introduction of known samples	I.R.	Mass Spect.	Approx. Yield at 600 P.	ϕ at 600 P.
P_1 $CH_3.CHO$	✓	✓				
P_2 $CH_3.CH_2.CHO$	✓	✓			43	0.001
P_3 $CH_3.CO.CH_3$	✓	✓	✓	✓	259	0.009
P_4  $(CH_3)_2CH.CHO$	✓	✓	✓	✓	392	0.0085
P_5 $CH_2 = C(CH_3).CHO$	✓	✓	✓	✓	497	0.014
P_6 $(CH_3)_3 C.OH$	✓	✓	✓	✓	111	0.002
P_7 $CH_3.CO.C_2H_5$	✓	✓				$\overset{\sim}{0.0005}$

FIG. 3.3.1

MASS SPECTRA OF PRODUCTS FROM THE REACTION Hg*/O_2 + 2-Methyl Propene

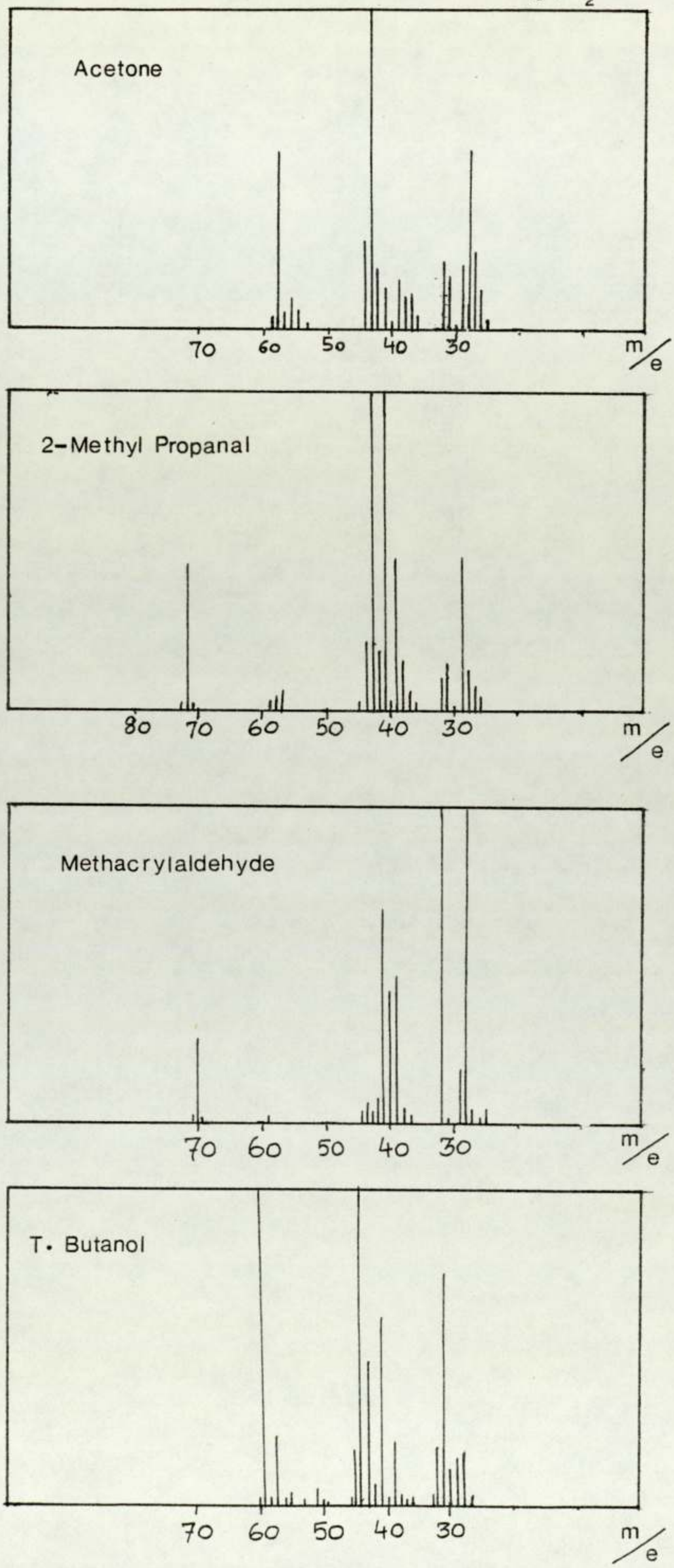
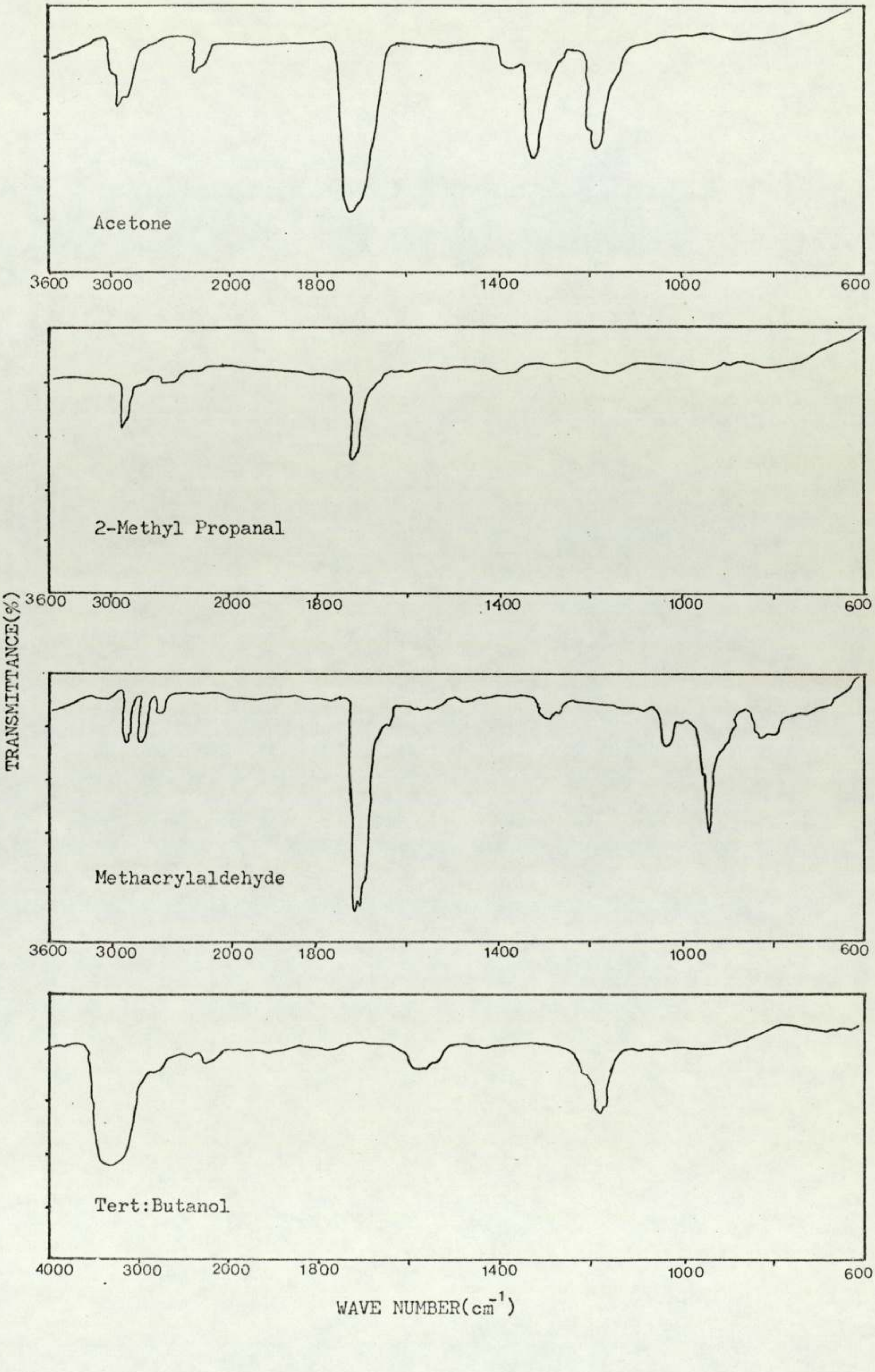


FIG. 3.3.2 INFRA-RED SPECTRA OF PRODUCTS FROM Hg^{*}/O_2+ 2-Methyl Propene



i.e. by means of the G.L.C. retention times and the introduction of known samples it was identified and was thought that the confirmation was sufficient.

3. Acetone.

This was one of the major products. It was collected during the high conversion runs. It was found to have the same retention time as that of a pure sample of it on the 4 m. di-n butylphthalate column.

Its mass spectrum is provided in the fig. 3.3.1. The molecular ion peak is at m = 58. The base peak at m = 43 is of the fragmentation ion CH_3CO^*, which is characteristic for most methyl ketones. The mass spectrum matched with that of an authentic sample of the pure compound. Further, its I.R. spectrum was taken as shown in fig. 3.3.2. It shows the typical carbonyl band at 1751 cm^{-1}.

4. 2-Methyl Propanal.

This compound was also separated and collected on a di-butyl phthalate column. It was found to give a characteristic $C = O$ stretching band at 1721 cm^{-1} and C-H stretching bands at 2940 cm^{-1} and 2810 cm^{-1}. It was found to have an empirical formula C_4H_8O by its mass spectrum. Its mass spectrum consisted of a peak at m = 29 and the characteristic m-1 peak at m = 71. The molecular ion peak is at m = 72. It was confirmed by comparing a mass spectrum of an authentic sample which matched unambiguously. Hence this compound was confirmed as 2-methyl propanal. Its retention time also matched with that of an authentic sample.

5. Methacrylaldehyde.

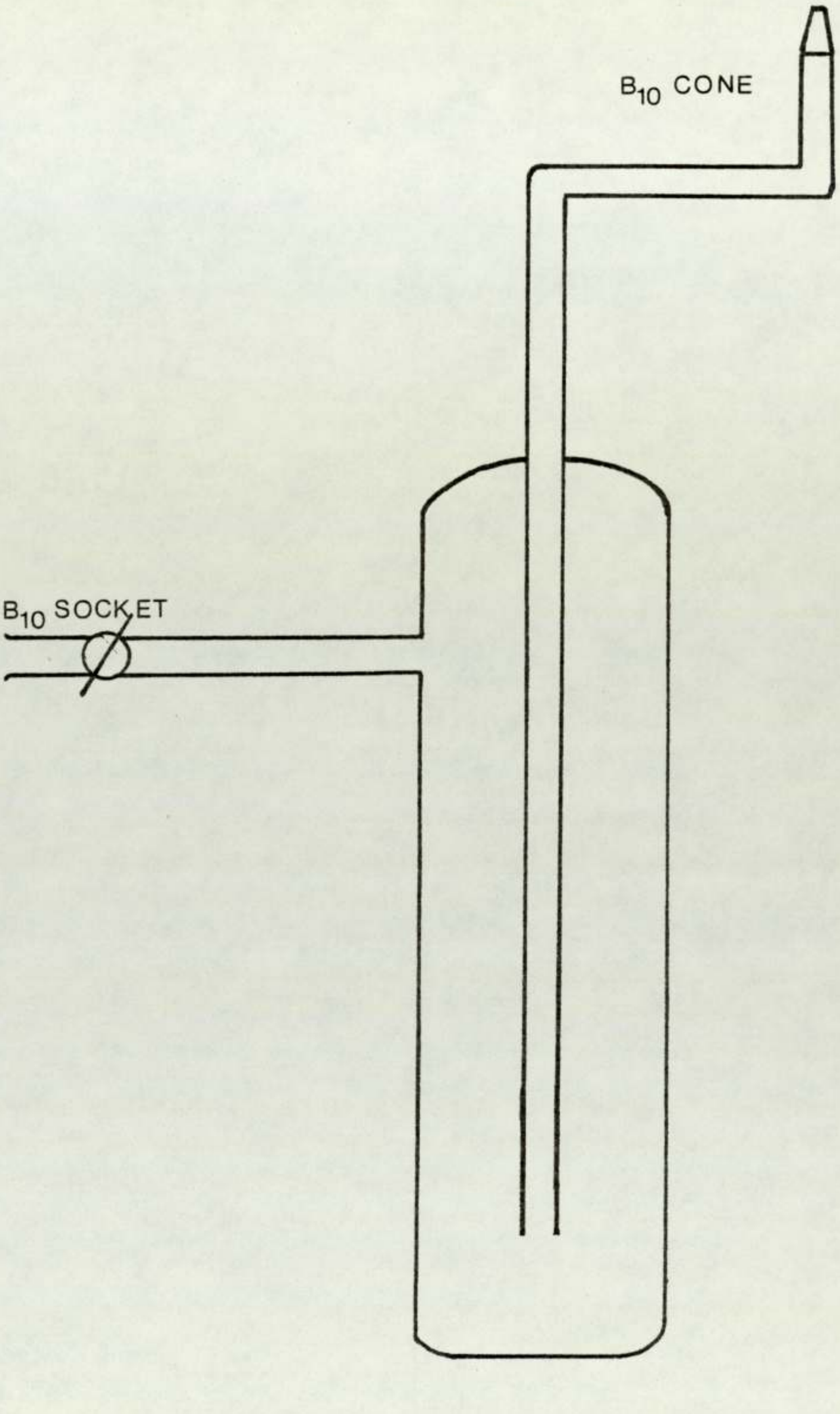
This compound is also a major product. It was collected during the high conversion runs on a 4 m. di butyl phthalate column. Its mass spectrum showed the molecular ion peak occuring at $m = 70$. An authentic sample of methacrylaldehyde was then taken and its mass spectrum was compared. It was found that the matching was unambiguous. The characteristic m-1 peak of aldehydes is at $m = 69$ as shown in the figure 3.3.1. An I.R. was also taken of the compound and it showed the typical C-H stretching bands at 2690 cm^{-1} and 2790 cm^{-1} and C = O stretching at 1726 cm^{-1}. It was also confirmed by its retention time and by the introduction of its authentic sample onto the G.L.C.

6. Tertiary Butanol.

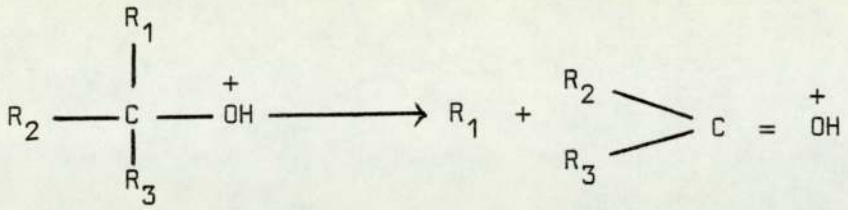
This compound presented some problems in the collection, as during the collection its elution on the G.L.C. seemed to be supressed and also because it usually solidifies at temperatures below 25^{0}C. However, warming the reaction mixture slowly and after removing half of the collection mixture it could be easily separated. It was collected and its mass spectrum and I.R. was taken. The characteristic band at 3400 cm^{-1} (as shown in fig. 3.3.2.) indicates the presence of an alcoholic or wet substance. Its mass spectrum matched with that of an authentic sample of it thus confirming it to be tertiary butanol.

In the mass spectrum, the molecular ion peak at $m = 74$ is not visible. Usually in tertiary alcohols the molecular ion peak is not detectable. The general fragmentation process involves cleavage of the bond beta to the oxygen atom. The largest group is lost most readily.

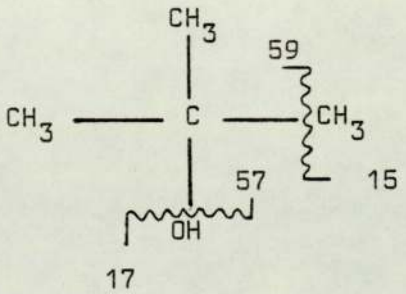
FIG. 3.4.1



TRAP FOR HYDROPEROXIDE DETECTION



The characteristic peaks at m = 57 and m = 59 are typical of tertiary butanol.



It was also confirmed through the G.L.C. retention times and by the introduction of a pure authentic sample onto the G.L.C. and noticing the peak size which increased.

7. 2-Butanone.

This product could not be collected for identification due to its very low yields even at high conversions. This was proved to be 2-butanone by means of its retention time and also when its pure sample was introduced in the system and a G.L.C. chromatogram was taken its peak size increased. There was no further need for its identification.

Unidentified Products

Three unidentified products with very short retention times were observed in the G.L.C. chromatogram. No attempts were made to identify these compounds. The first two were probably propane and propene whereas the third product which eludes within the main alkene peak seems to be formaldehyde.

3.4. HYDROPEROXIDE TESTS

As hydroperoxides are known to be among the products of hydrocarbon oxidations, and also molecular oxygen in at least one of its excited states is known to give hydroperoxides as a product with alkenes, hence it was thought necessary to check if there is any peroxide formation in our system. The ferrous thiocyanate method of hydroperoxide detection was used, which is modified by Egerton and others.(210, 211) The method is as follows.

5 gms. AR ammonium thiocyanate and 5 gms. AR ferrous sulphate are dissolved in 100 ml. of water containing 1 ml. of concentrated sulphuric acid. The solution is freed of its red colour by shaking it with amyl alcohol. Analysis is carried out by adding to 3 ml. of test solution one ml. of the reagent which develops maximum intensity and is compared on the spectrophotometer against a solution of one ml. of reagent in 3 ml. water.

To check for the presence of peroxides in the system, a special sample tube was constructed in the laboratory (as shown in fig. 3.4.1.). This could be easily connected to the mainline via the greaseless manifold through its B_{10} opening. When during any time a test for peroxide was needed for 2-methyl propene, the whole reaction mixture after the irradiation was freezed onto the small amount (10 - 12 mls.) of reagent already evacuated and freezed by means of liquid nitrogen around the sample tube. It was then very slowly allowed to warm up and to mix with the reagent. The presence of any peroxide immediately changes the colour to intense red.

In the case of 2-methyl propene, the test gave no positive results. It was repeated several times to detect any hydroperoxide formation in the system, but it always gave a negative result. Furthermore, when the identification of products was completed, it was found that there were no traces of peroxide or hydroperoxides amongst them, hence it was safe to assume that either the peroxides are not formed in our system or even if they are formed they decompose very quickly prior to their detection.

3.5. CALIBRATION RESULTS

It is important to calibrate the detector when most of the products have been identified so as to determine the absolute concentration of the products for various studies.

Although most of the compounds were available commercially and were purified in a manner described in 2.6 , but during the calibration runs some of the compounds, having very low vapour pressure and the tendency to solidify at the operating temperature, could not be calibrated. Hence their molar sensitivities were calculated relative to acetone. Methacrylaldehyde and acetone were calibrated by the method discussed in 2.2.(a). The measurements were carried out at low concentrations and the values of the detector calibration factor were calculated by the relation

$$P = f.A$$

The results of the calibration are summarized in Table 3.5.

TABLE 3.5.

CALIBRATION FACTORS.

Run No.	Pressure (mm) at 20.4 ± 3^{o}C		Mean Area of Peak at S = 1 x 10^{2} (arbitrary units)	Calibration factor
	In V_1(3.95 ml)	In R.S(760 ml)		
	(a) Methacrylaldehyde			
148	124	0.6444	121,00	5.32 x 10^{-5}
149	151	0.7848	149,99	5.23 x 10^{-5}
150	125	0.6496	118,82	5.46 x 10^{-5}
			Mean	5.33 x 10^{-5}

Calibration factor of Methacrylaldehyde = 5.33 ± 0.11 x 10^{-5}

Run No.	In V_1(3.95 ml)	In R.S(760 ml)	Mean Area of Peak at S = 1 x 10^{2} (arbitrary units)	Calibration factor
	(b) Acetone			
151	185	0.9615	133,90	7.18 x 10^{-5}
152	129	0.6704	99,45	6.73 x 10^{-5}
153	172	0.8939	161,35	5.53 x 10^{-5}
			Mean	6.48 x 10^{-5}

Calibration factor of Acetone = 6.48 ± 0.3 x 10^{-5}

FIG. 3.7.1

TIME DEPENDENCE STUDIES AT HIGH PRESSURE

(Hg^*/O_2 + 2-Methyl Propene)

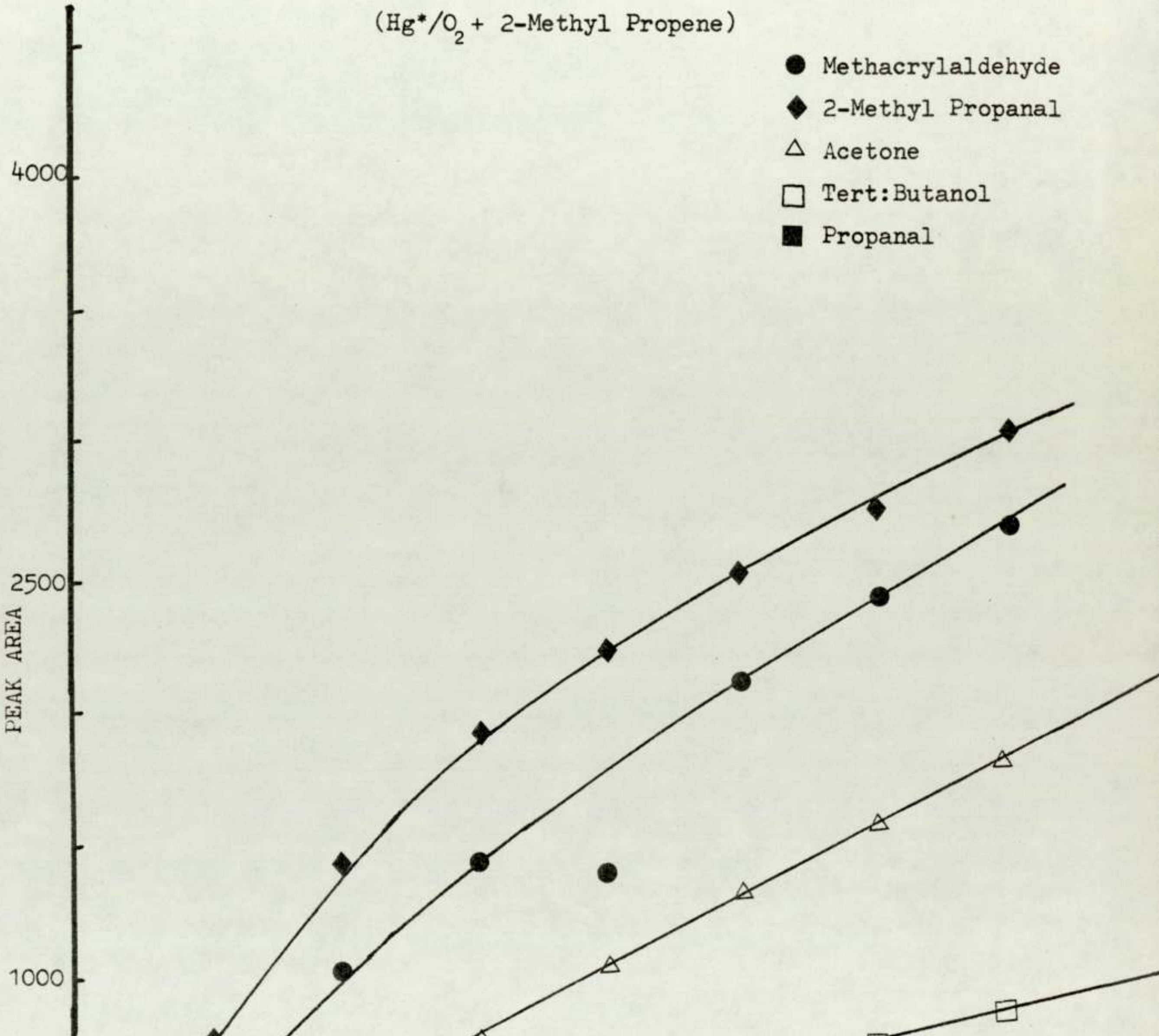
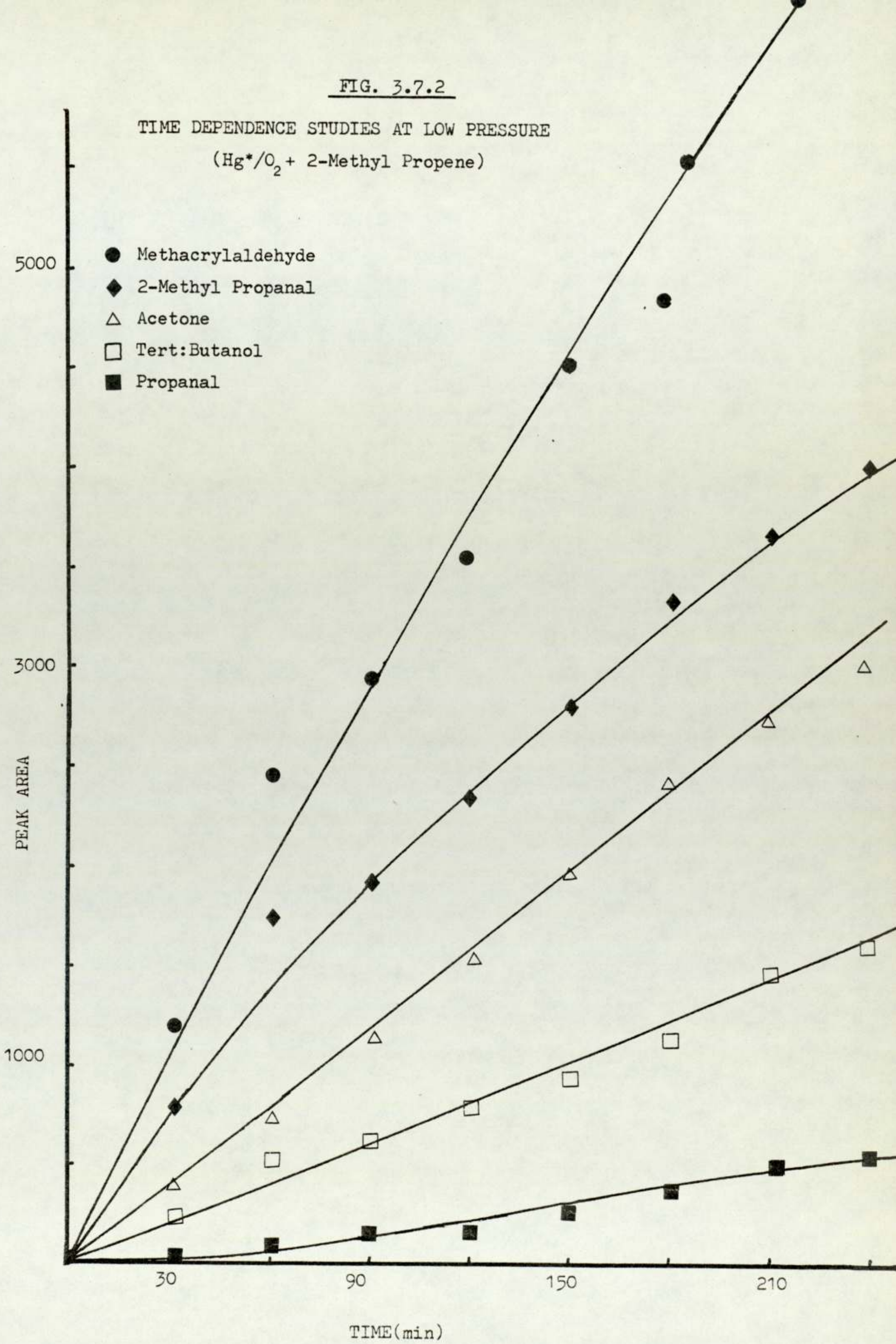


FIG. 3.7.2


TIME DEPENDENCE STUDIES AT LOW PRESSURE
(Hg^*/O_2 + 2-Methyl Propene)
● Methacrylaldehyde
◆ 2-Methyl Propanal
△ Acetone
□ Tert:Butanol
■ Propanal
5000
3000
1000
PEAK AREA
30
90
150
210
TIME(min)

3.6 QUANTUM YIELDS

Quantum yields of the products can be calculated from the relation

$$\emptyset = \frac{\text{Yield of Product}}{\text{No. of light quanta absorbed}}$$

Measurements were made relative to $\emptyset$ for Hg^*/N_2O reaction which is known to be one.

Runs with nitrous oxide were occasionally carried out under the same conditions and nitrogen yield was measured from it. The product yield was calculated as follows -

If a peak of calibrant area A_1 units is observed, then the number of moles of A_1 in the reaction system can be given by

$$C_1 = A_1 f_1$$

where f_1 is the calibration factor. The glc was calibrated with authentic samples of the materials, where available. In other cases, glc calibration factors were estimated.(212)

3.7 EFFECT OF IRRADIATION TIME

Two separate runs were performed to study the variation in the yields of major and minor products with irradiation time. In one run, the total pressure was kept high (700 mm.). Rest of the conditions were similar as for a normal run. Product yields were noted at each 30 minutes up to a period of 240 minutes. The results are plotted in figures 3.7.1 and 3.7.2. The fig. 3.7.1 gives the yield in peak areas plotted versus time and the fig. 3.7.2

FIG. 3.8.1 EFFECT OF PRESSURE VARIATION (Hg^*/O_2 + 2-Methyl Propene)

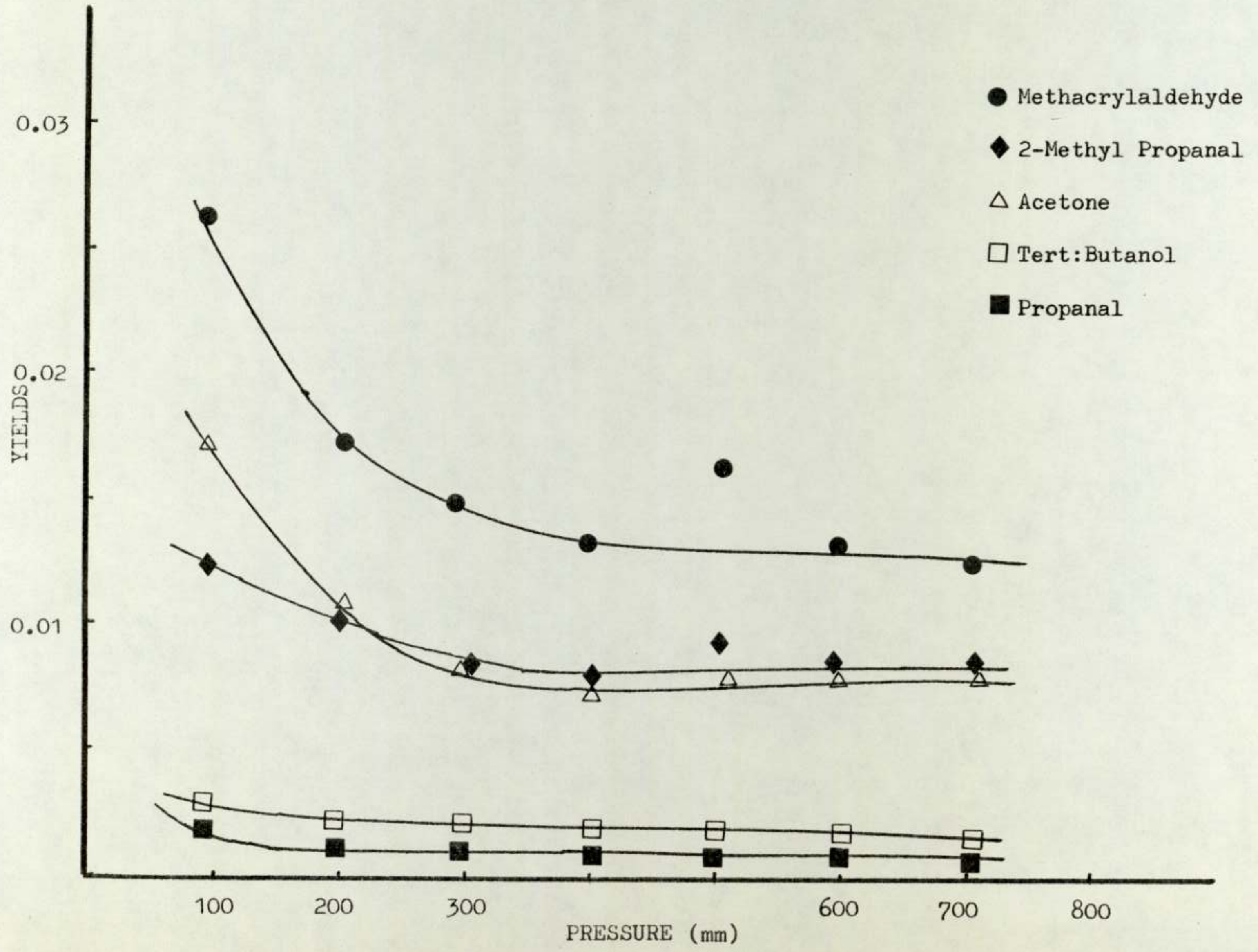
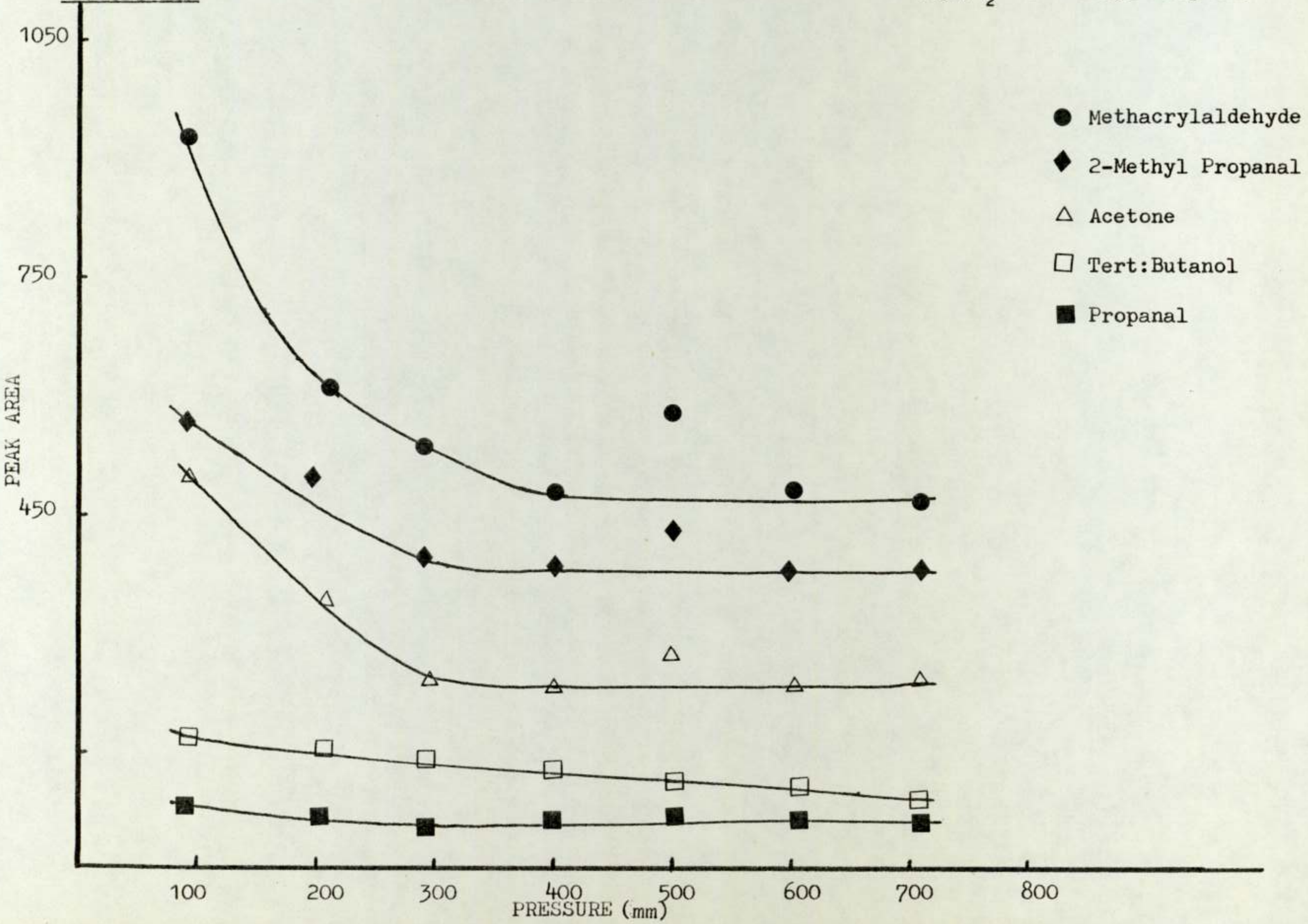


FIG. 3.8.2 EFFECT OF PRESSURE VARIATION (Hg^*/O_2 + 2- Methyl Propene)



shows the peak areas against time at low pressure. The following observations can be made.

(a) At High Pressure

All the products show a linear variation with the increase of time. The rate of formation of 2-methyl propanal seems to fall off after a certain time. The rate of formation of methacrylaldehyde also seems to fall off slightly at higher conversions.

(b) At Low Pressure

All the products show a linear increase with time. The rate of formation of 2-methyl propanal again seems to fall off after a certain time. The yield of propanal shows some increase with respect to time.

3.8 EFFECT OF PRESSURE VARIATION

During the study the range of total pressure investigated was 100 ⟶ 700 mm. Ratios of alkene to oxygen was always kept in excess of 1 : 10. All the reactions were at room temperature 18 ± 3°C. Rest of the conditions were same as in the normal runs. The variation of quantum yield ϕ with total pressure for the products are shown in the fig. 3.8.1. A plot of peak areas versus total pressure is also given in fig. 3.8.2. Following points can be said regarding the general trend of both major and minor products towards total pressure.

3.8.(a) Major Products.

The quantum yields of the major products show a definite decrease as the total pressure is increased. After a certain pressure is reached (P = 300) in the case of acetone and 2-methyl propanal and (P = 400) in case of methacrylaldehyde, the quantum yield appears to be steady, i.e. showing little dependence on further increase in pressure.

3.8.(b) Minor Products.

The quantum yields of the minor products show little dependence on pressure. Tertiary butanol shows some pressure dependence as its quantum yield appears to decrease slightly with the increase of pressure. 2-butanone and propanal show very little dependence on pressure. Their quantum yields being almost constant throughout the pressure range. The quantum yields ϕ of products at various pressures are given below in the Table 3.8. The quantum yields are calculated by using the values of the detector calibration factors in Table 3.5.

TABLE 3.8.

Pressure (mm)	CH_3CH_2CHO	CH_3COCH_3	$\begin{matrix}CH_3\\CH_3\end{matrix}{>}CH.CHO$	$CH_2{=}C(CH_3).CHO$	$(CH_3)_3.COH$	$CH_3COC_2H_5$
99	0.0019	0.0170	0.0123	0.0265	0.0030	< 0.0005
210	0.0013	0.0112	0.0108	0.0174	0.0026	
292	0.0010	0.0084	0.0083	0.0150	0.0024	
401	0.0010	0.0078	0.0082	0.0138	0.0020	
506	0.0012	0.0102	0.0096	0.0173	0.0020	
595	0.0011	0.0080	0.0085	0.0139	0.0019	
709	0.0011	0.0090	0.0084	0.0128	0.0016	

The quantum yield of 2-butanone was not calculated due to the inaccuracy in measuring very small peaks. It can be seen that the total quantum yield of all the products varied between 0.06 - 0.033. There may be some errors due to the uncertainty in the calibration

FIG. 3.9.1

EFFECT OF ALKENE/O_2 RATIO ON PRODUCT YIELDS AT HIGH PRESSURE
(Hg^*/O_2 + 2-Methyl Propene)

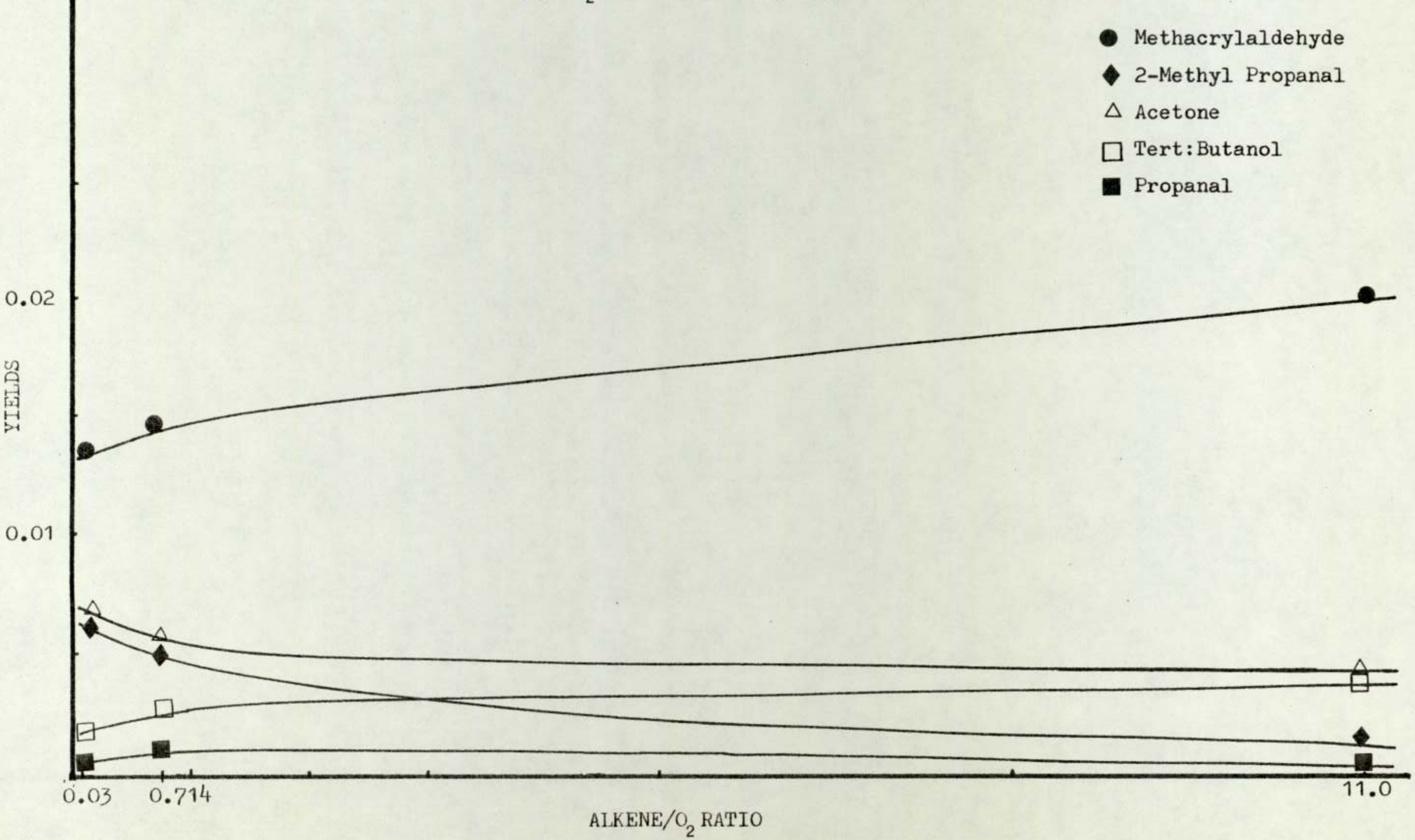
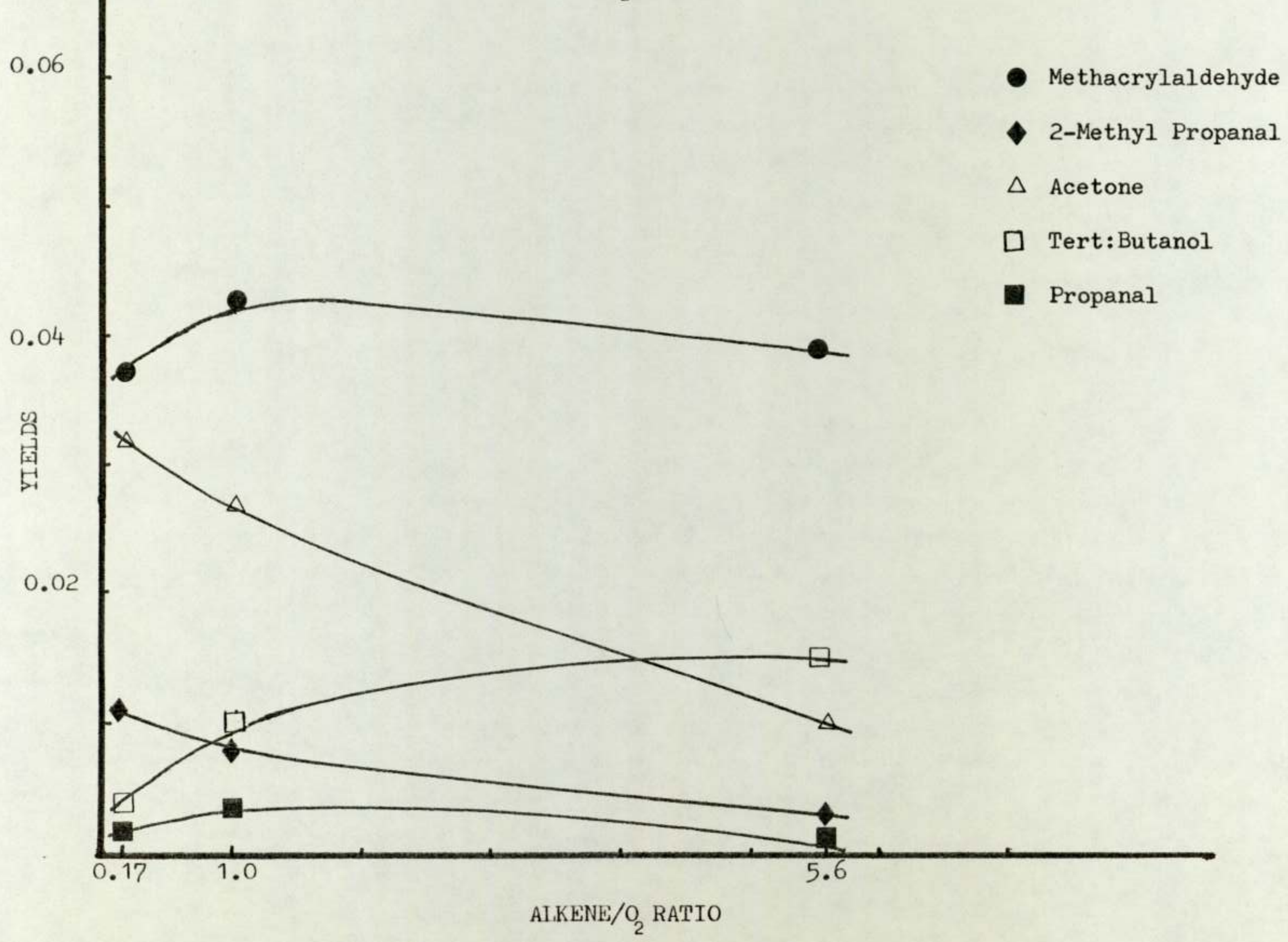


FIG. 3.9.2

EFFECT OF ALKENE/O_2 RATIO ON PRODUCT YIELDS AT LOW PRESSURE

(Hg^*/O_2 + 2-Methyl Propene)



factors and the inaccuracy in measuring small and overlapping peaks.

3.9 EFFECT OF ALKENE/O_2 RATIO

All the runs were carried out at room temperature 18 ± 3°C. The ratio of alkene to oxygen was varied at both high and low pressures. The variations in quantum yields with different alkene/O_2 ratio are given in Table 3.9 below.

TABLE 3.9.

Quantum yields of products at high pressure.

PC_4H_8/O_2		Quantum Yields					
mm.Hg	Ratio	$CH_3.CH_2.CHO$	CH_3COCH_3	$\begin{matrix}CH_3\\CH_3\end{matrix}\!>CH.CHO$	$CH_2=C(CH_3).CHO$	$(CH_3)_3.COH$	$CH_3COC_2H_5$
20/580	0.034	0.00044	0.0068	0.0063	0.0135	0.0019	0.0001
250/350	0.714	0.00075	0.0063	0.0052	0.0148	0.0029	0.0001
550/50	11.0	0.00040	0.0043	0.0016	0.0215	0.0039	0.0002

At low pressure

15/85	0.176	0.0018	0.032	0.011	0.037	0.0044	0.0003
50/50	1.0	0.0039	0.027	0.008	0.043	0.010	0.0004
85/15	5.6	0.0007	0.010	0.003	0.039	0.015	0.0002

Variation of quantum yields with the different alkene/O_2 ratios are also shown in fig. 3.9.1 and fig. 3.9.2.

The main points evident from the study are as follows -

1. The quantum yields of the products are greater in the low pressure runs.
2. The quantum yield of tertiary butanol increases in the presence of

a large excess of alkene. The quantum yield of methacrylaldehyde also show some increase, during the large excess of alkene in the system.

3. The yields of 2-methyl propanal and acetone show definite decrease when the alkene/O_2 ratio increases in the system.

Due to the very low yields and hence the difficulties observed in measuring the peak areas of the minor products, it is difficult to speculate about their trend towards the effect of alkene/O_2 ratio.

3.10 EFFECT OF REDUCED LIGHT INTENSITY

In order to see whether reducing the light intensity does have any marked effect on the quantum yields of the products, two separate experiments were performed. The difference between the two was of total pressure. In one experiment, the pressure was kept at 600 mm., whereas the other was confined to a total pressure of 100 m.m. All other conditions were the same as were in the pressure dependence studies.

The intensity of light was reduced by using only one lamp and furthermore a thin double layer of copper gauze was kept in between the lamp and the reaction cell window. This arrangement further reduced the intensity of radiation upon the reaction cell window. The transmittance of the gauze at 253.7 n m was previously been measured as 13% on a SP 700 UV spectrophotometer. Any reduction in the incident radiation intensity can be easily measured by comparing the reduction in the yield of N_2 from nitrous oxide run measured in the toepler system. The pressure of N_2 measured during

0·49

a run of five hours was found to be = 0.4875 mm. which corresponded to light intensity of 5.2% compared with a standard run.

The results are given in Table 3.10 and are compared with the results of a run of normal light intensity at about the same pressure keeping all other conditions similar.

TABLE 3.10

Effect of Reduced Light Intensity on Product Yield.

Irradiation time (min)	Total Pressure mm.	Propanal	Acetone	2-methyl propanal	Methacryl aldehyde	Tert. Butanol	2-Butanone
300	520	0.0014	0.0103	0.040	0.023	0.002	-
*300	512	0.0012	0.0102	0.0096	0.0173	0.0020	
300	100	0.0016	0.015	0.052	0.038	0.0048	
*300	102	0.0018	0.017	0.012	0.027	0.0045	

* Indicates runs with normal light intensity

From the results, it can be said that reducing the light intensity does have some effect on the ϕ of some of the products. As can be seen from Table 3.10 the quantum yield of 2-methyl propanal increases. There is little increase in the yield of methacrylaldehyde whereas there is very little or no effect on the quantum yields of rest of the products on reducing the light intensity.

3.11 EFFECT OF ADDED NITROUS OXIDE

During two standard runs most of the oxygen was removed after the completion of five hours irradiation time. A glc chromatogram was taken at this stage and then nitrous oxide to the required pressure range was introduced in the system. The whole reaction mixture was then irradiated for ten minutes. At this stage again a glc chromatogram was taken. Quantum yields were then calculated before and after the ten minutes irradiation time. The results are given in Table 3.11.

TABLE 3.11

Effect of added nitrous oxide on the quantum yields.

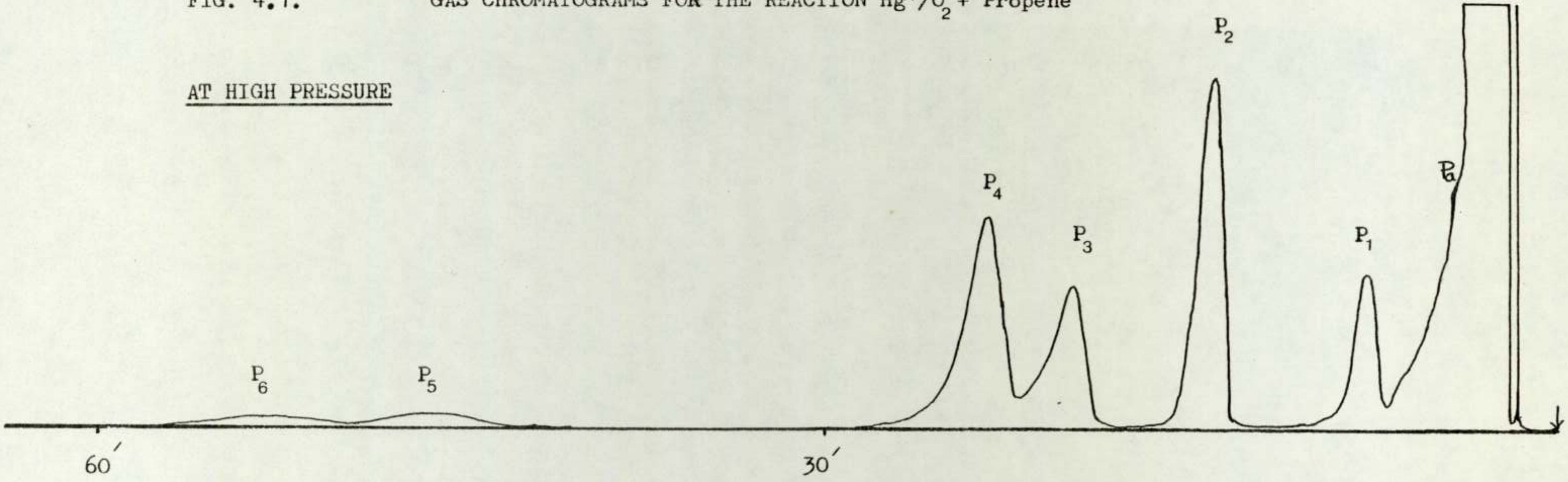
Irradiation time (min)	Pressure (mm)	Quantum Yields					
		Propanal	Acetone	2-methyl propanal	Methacryl-aldehyde	Tert. Butanol	2-Butanone
300	703	0.000185	0.0132	0.0029	0.0032	0.00021	0.00015
*310	706	0.00020	0.022	0.0068	0.0031	0.00020	0.00041
300	82	0.0005	0.011	0.0069	0.013	0.0012	0.00086
*310	85	0.0005	0.020	0.014	0.014	0.0012	0.0021

* Indicates run with a further irradiation of 10 in presence of N_2O.

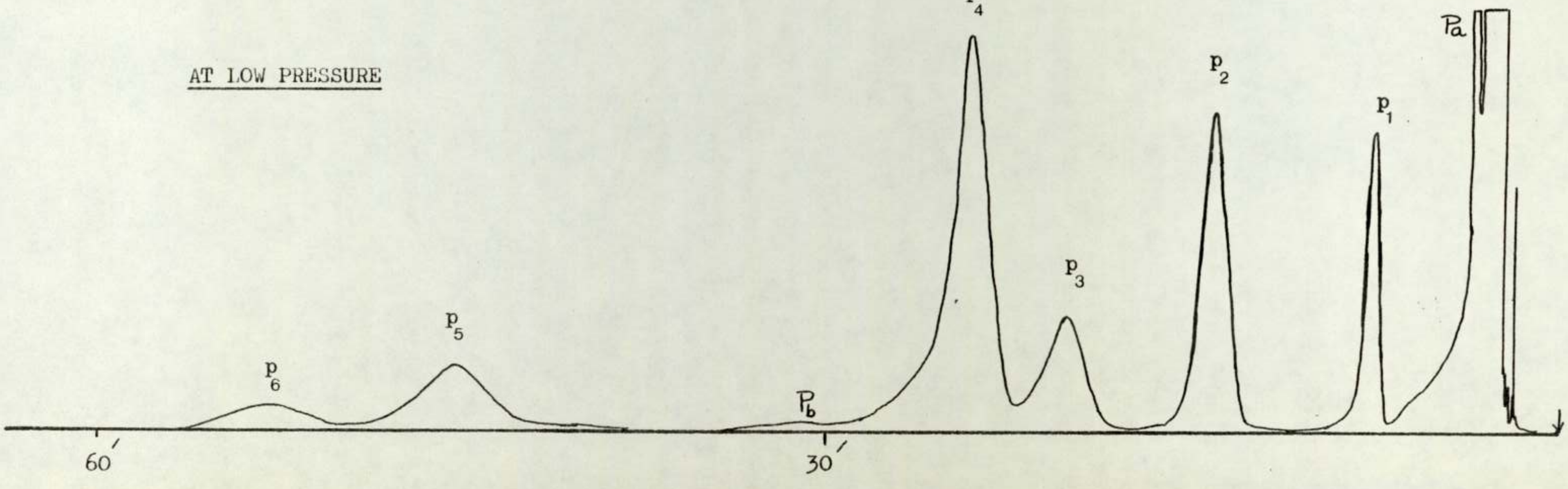
The results show that there is a change in the quantum yields of some of the products when irradiated in the presence of nitrous oxide. The quantum yields of 2-methyl propanal and 2-butanone increases. Acetone quantum yield also increases, whereas the quantum yields of rest of the products do not show any apparent change.

FIG. 4.1. GAS CHROMATOGRAMS FOR THE REACTION Hg^*/O_2 + Propene

AT HIGH PRESSURE



AT LOW PRESSURE



CHAPTER FOUR

RESULTS FOR MERCURY PHOTOSENSITIZED OXIDATION WITH PROPENE AND BUTENE-1

4.1 CHROMATOGRAMS FOR PROPENE

Chromatograms for propene at both high and low pressure are presented in fig. 4.1. Irradiation time during a standard run was three hours. All studies were made at room temperature 18°C ± 3°C. Column used throughout the reaction study was a 4 meter di-n-butyl phthalate with 2% Carbowax. Gas pressures for the GLC were -

P_{N_2} (carrier gas) ⟶ 30 lbs./in^2

P_{H_2} ⟶ 28 lbs./in^2

P_{Air} ⟶ 30 lbs./in^2

The symbols used in the chromatograms and elsewhere for the products are as explained below.

'P_1' represente the product Acetaldehyde.

'P_2' represente the product 1-2 Epoxy propane.

'P_3' represents the product Propanal.

'P_4' represents the product Acrylaldehyde.

'P_5' represents the product Methacrylaldehyde.

'P_6' represents the product 2-Butanone.

P_a and P_b represent unidentified product. They correspond to less than 2 % of the main products at high pressure ∼ 700 m.m. P_a was probably formaldehyde. CO, CO_2 and H_2O may have been present among the products, but were not specifically looked for.

4.2 IDENTIFICATION AND ANALYSIS OF PRODUCTS

Using the methods of analysis as explained in Section 2.5, the products identified are listed in Table 4.2. The different techniques used for the identification are also summarized.

The products with a superscript are the major products which were isolated by GLC from high conversion runs. The minor products were not isolated because of their very low yields and were confirmed by other alternative techniques. Brief notes are provided below for each of the individual compounds.

(P_1) Acetaldehyde.

Acetaldehyde was a major product. Its peak occurred just after the main alkene peak, which made it difficult to collect for I.R. and Mass Spect. It was however identified by the retention time on different columns. A pure sample of acetaldehyde was taken and a small amount ($<$ 1 mm.) was added to the reaction mixture and mixed according to the procedure described in Section 2.5. When a chromatogram was taken afterwards, the acetaldehyde peak increased very prominantly, thus confirming it to be acetaldehyde.

TABLE 4.2.

Identification of the Products from Propene

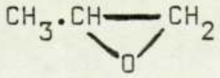
PRODUCTS	Identification Methods					
	G L C Ret. Times	By Introduction of known samples	I.R.	Mass Spect.	Approx. Yield at 500 mm.	ϕ at 500 mm.
P_1^* $CH_3.CHO$	✓	✓			107.5	0.006
P_2^*  $CH_3.CH\underset{O}{—}CH_2$	✓	✓	✓	✓	495.8	0.011
P_3^* $CH_3.CH_2.CHO$	✓	✓		✓	186.4	0.009
P_4^* $CH_2 = CH.CHO$	✓	✓		✓	525	0.034
P_5 $CH_2= C(CH_3).CHO$	✓	✓	✓	✓	34.1	0.001
P_6 $CH_3.CO.C_2H_5$	✓	✓			16.9	0.0005

FIG. 4.2.2

MASS SPECTRA OF PRODUCTS FROM THE REACTION Hg*/O_2 + Propene

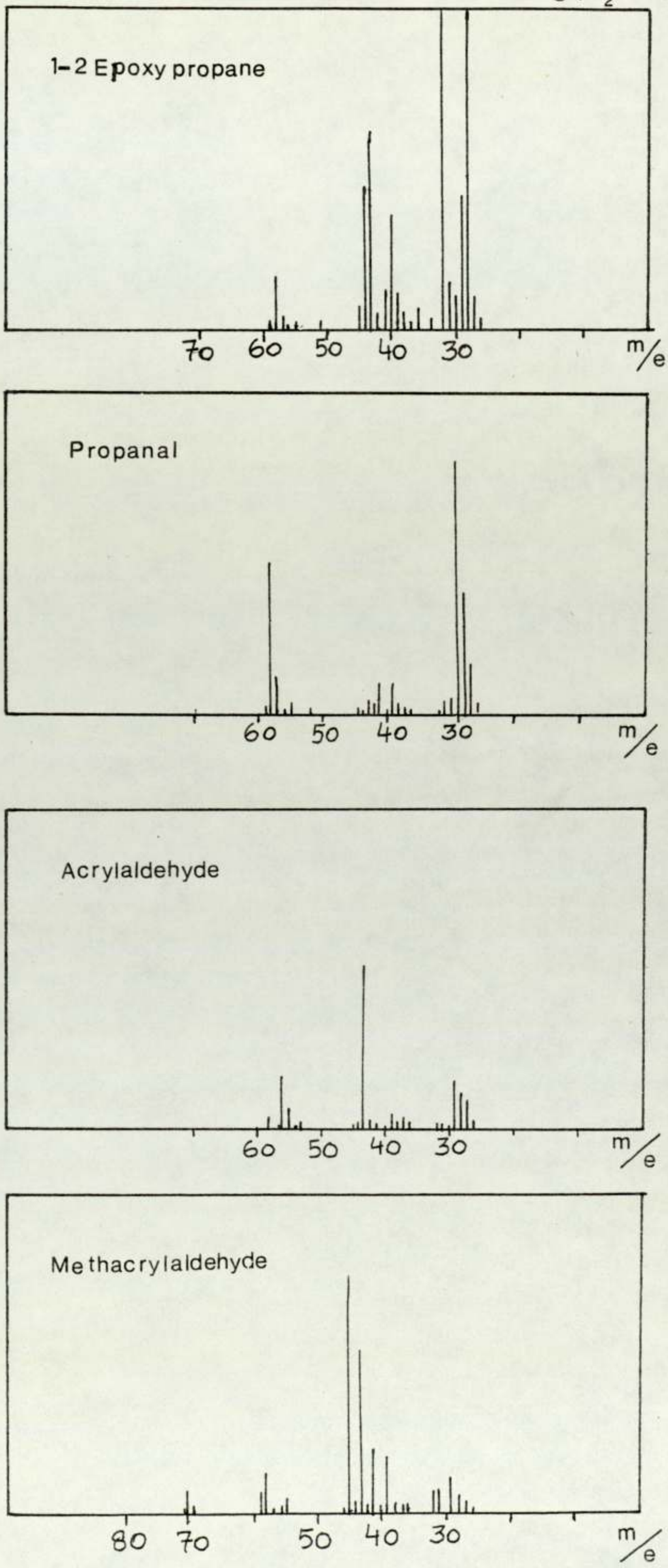
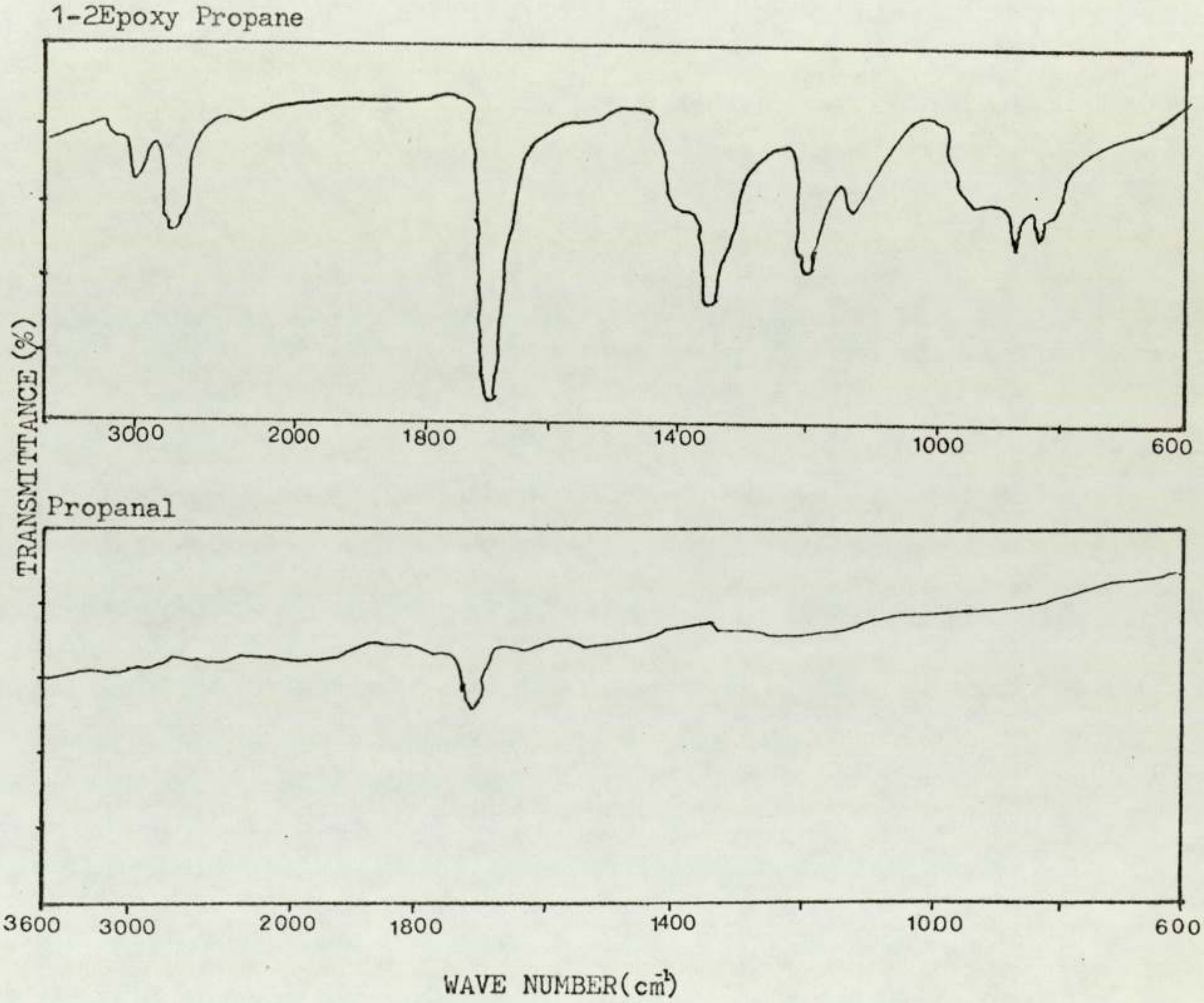


FIG. 4.2.3.

INFRA-RED SPECTRA OF PRODUCTS FROM Hg*/O + Propene



(P_2) 1 - 2 Epoxy Propane

This was also a major product. It was collected during the high conversion runs. It was found to have the same retention time as that of a pure sample of it on the dibutylphthalate column.

Its I.R. and mass spectrum were was taken. Its mass spectrum was compared with an authentic sample of 1-2 epoxy propane. Both spectrograms matched each other. The results are given in the fig. 4.2.2. The molecular ion peak is at m = 58.

(P_3) Propanal

This compound was also separated and collected for the mass spect. and I.R. The results are provided in fig. 4.2.3. The mass spectrum matched with that of an authentic sample. The molecular ion peak is at m = 58 with another (m-1) peak at m = 57 characteristic of aldehydes. It was also confirmed by the retention time and by the introduction of its sample in the glc and measuring the peak size.

(P_4) Acrylaldehyde

This compound was also collected during high conversion runs. It was confirmed by comparing its retention time and by introducing a known sample in the reaction mixture and measuring the peak size which increased. Its mass spectrum matched with that of an authentic sample of it.

(P_5) Methacrylaldehyde

This product was also collected during high conversion runs. Its retention time matched with that of an authentic sample. Its peak size increased when a small amount of its pure sample was introduced in the reaction mixture and glc chromatogram was taken.

Its mass spectrum matched with the mass spect. of an authentic sample of it, showing the molecular ion peak at m = 70.

(P_6) 2-Butanone

This compound could not be collected due to very low yields even at high conversion runs. It was confirmed by comparing its retention time with that of a pure sample of it. Also when its pure sample was introduced in the reaction system ($<$ 1 mm.) and after a thorough mixing, a chromatogram was taken, it was found that its peak size increased, thus proving it to be 2-butanone.

Products P_a and P_b remained unidentified due to very low yields and short retention times. Product P_b was probably formaldehyde.

4.3 CALIBRATION RESULTS

The four major products after the identification were calibrated by the method discussed in section 2.2.(a). The results of the calibration are summarized in Table 4.3. Those products which were not calibrated, their molar sensitivities were calculated relative to 1-2 Epoxy Propane, as described previously.

TABLE 4.3.

CALIBRATION FACTORS

Run No.	Pressure (mm.) at 20.4 ± 3°C		Mean Area of Peak at s = 1 × 10^2 (arbitrary units)	Calibration factor
	In V_1(5.30 ml)	In R.S(773 ml)		
	(a) Acrylaldehyde			
140	141	0.9668	12,847.0	7.5×10^{-5}
141	125	0.8570	11,115.0	7.71×10^{-5}
142	112	0.7679	9,488.0	8.09×10^{-5}
			Mean =	7.76×10^{-5}
Calibration factor of Acrylaldehyde = 7.76×10^{-5}				
	(b) 1-2 Epoxy Propane			
140	182	1.2479	56,235.0	2.21×10^{-5}
141	127	0.8707	31,096.0	2.80×10^{-5}
142	77	0.5279	15,408.0	3.40×10^{-5}
			Mean =	2.80×10^{-5}
Calibration factor of 1-2 Epoxy Propane = 2.80×10^{-5}				
	(c) Acetaldehyde			
150	84	0.5759	8,845.0	6.51×10^{-5}
151	112	0.7679	10,815.0	7.1×10^{-5}
152	79	0.5416	7,849	6.9×10^{-5}
			Mean =	6.83×10^{-5}
Calibration factor of Acetaldehyde = 6.83×10^{-5}				
	(d) Propanal			
150	76	0.5210	9,326.0	5.58×10^{-5}
151	93	0.6376	10,452.0	6.10×10^{-5}
152	87	0.5965	10,110.0	5.90×10^{-5}
			Mean =	5.86×10^{-5}
Calibration factor of Propanal = 5.86×10^{-5}				

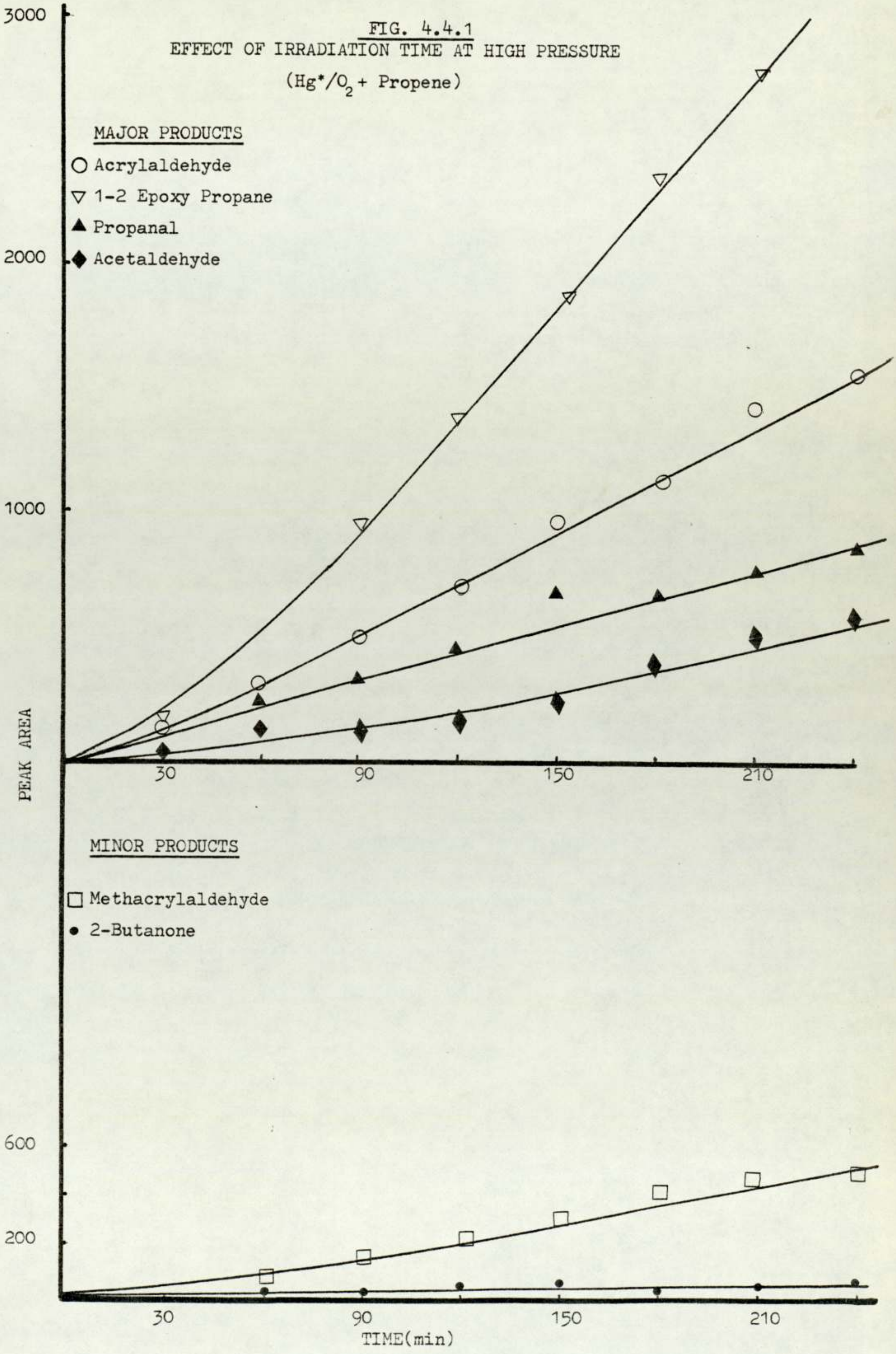


FIG. 4.4.1
EFFECT OF IRRADIATION TIME AT HIGH PRESSURE
(Hg^*/O_2 + Propene)

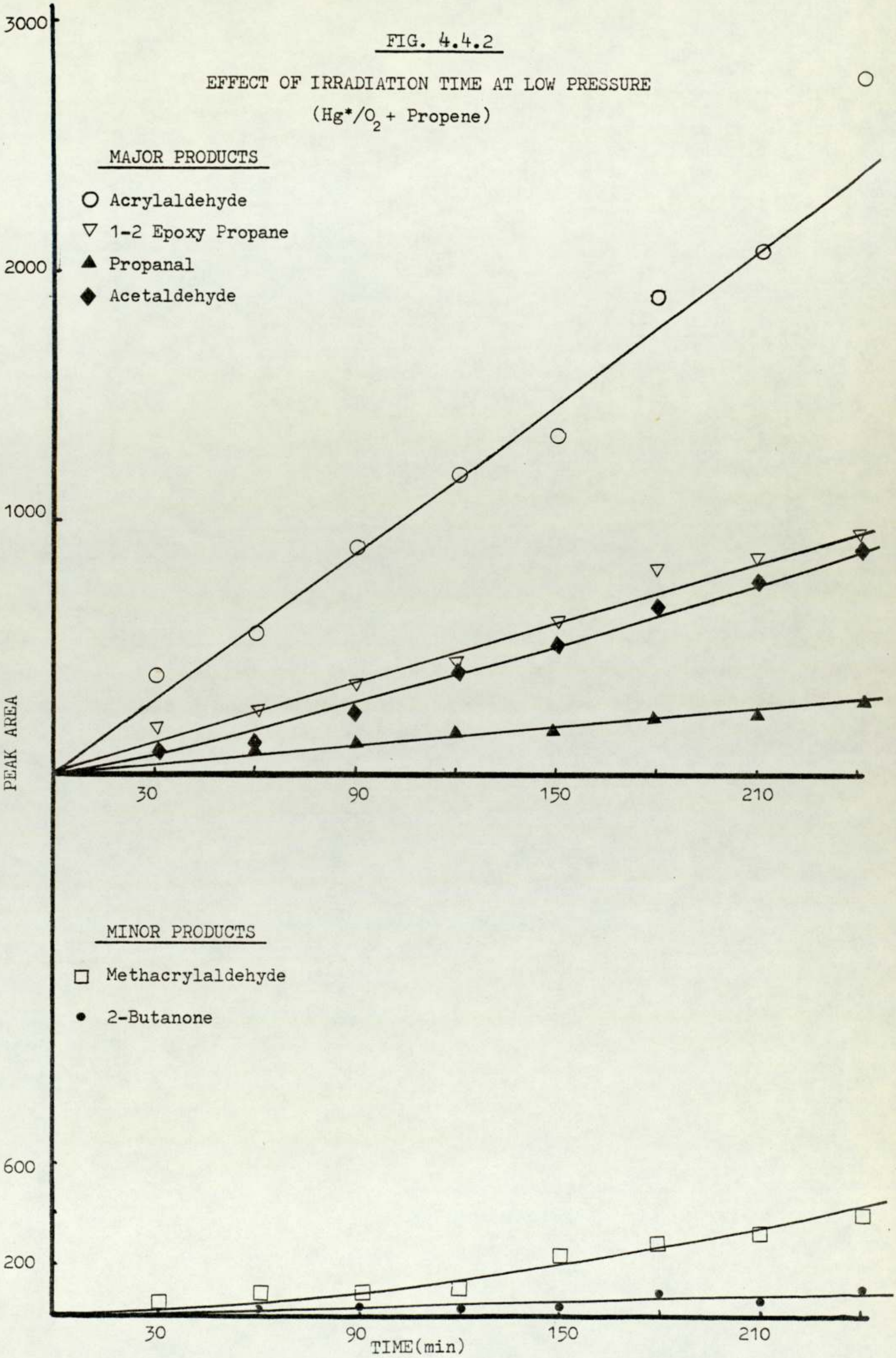


FIG. 4.4.2

EFFECT OF IRRADIATION TIME AT LOW PRESSURE

(Hg^*/O_2 + Propene)

4.4 EFFECT OF IRRADIATION TIME

The results of time dependence of the products arising from the Hg^*/O_2 + propene reaction at room temperature 18 ± 3°C are shown in figures 4.4.1 and 4.4.2. The top graph in both the figures show the time dependence of major products at high and low pressure, whereas the lower graphs show the dependence of minor products with respect to time. The following points can be made.

(a) Major Products

In the high pressure runs during the early time period (up to 1 hour), the yields of all major products show a linear variation with time, after 60 minutes the rate of formation seems to be increased. In the low pressure runs the yields of all the major products seem to increase linearly with time. The yields of acetaldehyde in both high and low pressure runs show definite increase with time.

(b) Minor Products

The yield of methacrylaldehyde seems to increase with time. During the early time period, it shows little increase, whereas the yield of 2-butanone does not seem to vary much with time.

4.5 EFFECT OF PRESSURE VARIATION

During the study, the range of total pressure investigated was from 100 to 700 m.m. All the reactions were performed at room temperature, i.e. 18 ± 3°C. Rest of the conditions were same as in the standard runs.

The variation of quantum yields with total pressure for the products are shown in the figure 4.5.1. A plot of peak areas

FIG. 4.5.1 EFFECT OF PRESSURE VARIATION (Hg^*/O_2 +Propene)

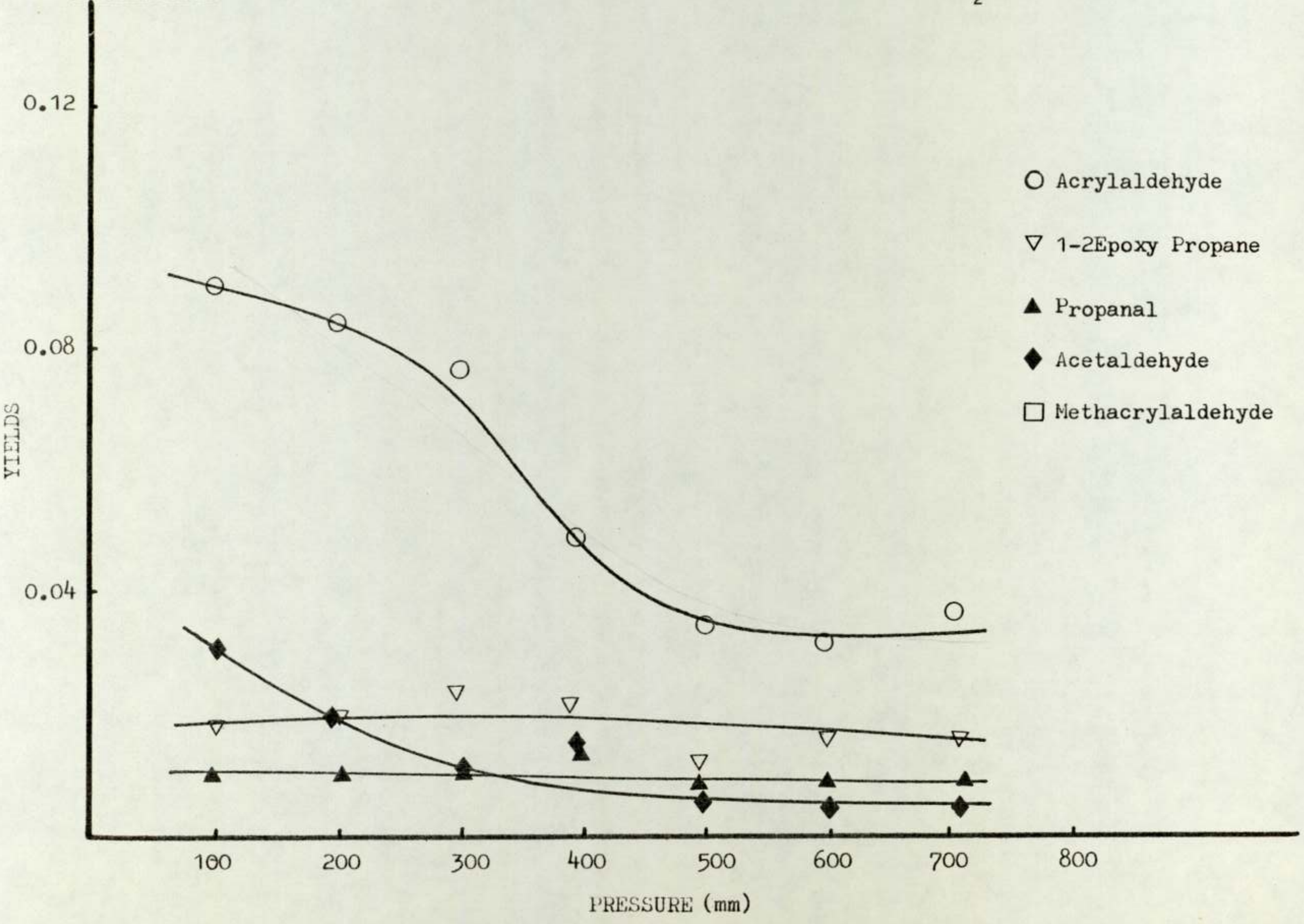
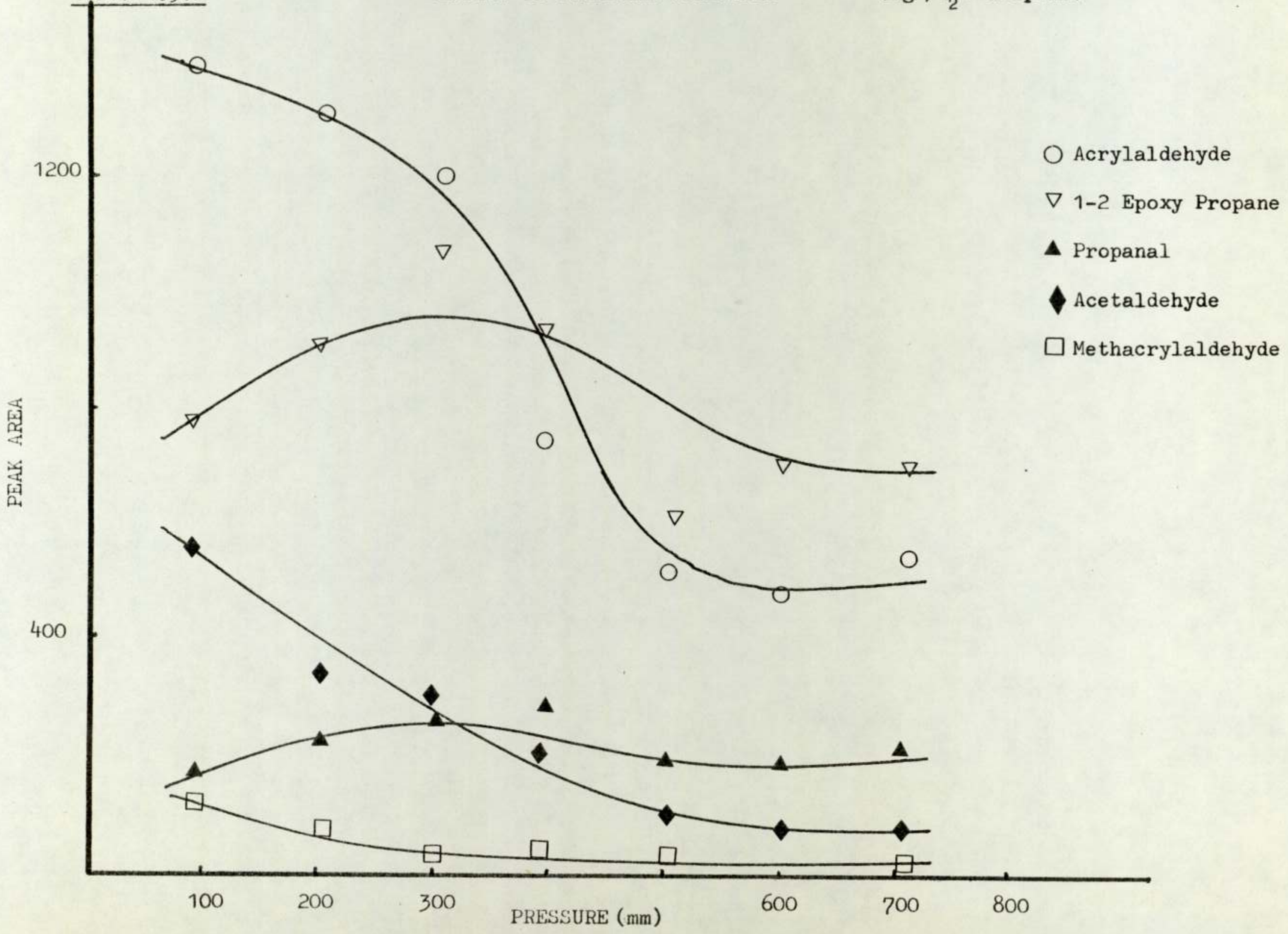


FIG. 4.5.2

EFFECT OF PRESSURE VARIATION (Hg*/O_2 + Propene)



versus total pressure is also supplied in fig. 4.5.2.

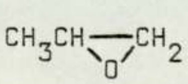
Following points can be made regarding the general behaviour of both major and minor products towards total pressure.

The quantum yield of acetaldehyde decreases with increasing pressure. The yield of acrylaldehyde also decreases with increasing pressure, though in a more complex way. Above about 500 m.m. pressure the quantum yields of all the major products appear to be steady, i.e. shows very little dependence on further increase in pressure. From the figure, it seems that the epoxide and the propanal yield have little dependence on pressure. Their quantum yields seem to be steady with pressure within the experimental error.

The quantum yields of the minor products show little dependence on pressure. The quantum yields of products at various pressures are given in the Table 4.5. The quantum yields are calculated in a manner described in section 3.6 and making use of the calibration factors described in section 4.3.

TABLE 4.5.

Variation of quantum yield with pressure

Pressure (mm)	$CH_3.CHO$	 $CH_3CH\underset{O}{—}CH_2$	$CH_3CH_2.CHO$	$CH_2=CH.CHO$	$CH_2=C(CH_3).CHO$	$CH_3CH_2OCH_3$
103	0.031	0.018	0.008	0.090	0.0076	0.0002
206	0.018	0.021	0.011	0.085	0.0034	0.0005
309	0.011	0.025	0.013	0.078	0.0015	0.00049
397	0.017	0.022	0.014	0.048	0.0019	0.0006
502	0.006	0.011	0.009	0.034	0.0015	0.0005
603	0.004	0.016	0.009	0.032	0.0011	0.0004
711	0.004	0.016	0.012	0.038	0.00087	0.00038

It can be seen that the total quantum yield of all the products varied between 0.15 - 0.06. The errors may be due to the uncertainty in the calibration factors and the inaccuracy in measuring small and overlapping peaks.

4.6 EFFECT OF REDUCED LIGHT INTENSITY

To study the effect of reduced light intensity the reaction mixture in a high pressure ($P \sim 600$ m.m.) run was irradiated at a lower light intensity. All other conditions were same as in the normal runs. The light intensity was reduced by using only one lamp and furthermore a thin double layer of copper gauze was kept in between the lamp and the reaction cell window. This arrangement further reduced the intensity of radiation upon the reaction cell. The transmittance of the gauze at 253.7 n.m. had previously been measured as 12.5% on a SP 700 UV spectrophotometer.

Any reduction in the incident radiation intensity can be easily measured by comparing the reduction in the yield of nitrogen from the nitrous oxide run measured in the toepler system.

The pressure of nitrogen measured during a run of three hours was found to be = 0.1009 m.m., which corresponded to light intensity of 9.5 % compared with a standard run.

The results are given in Table 4.6 and are compared with the results of a run of normal light intensity at about the same pressure, keeping all other conditions similar.

TABLE 4.6.

Effect of Reduced Light Intensity on Quantum Yields

Irradiation time (min.)	Pressure mm	Quantum Yields			
		$CH_3.CHO$	$CH_3.CH\underset{O}{—}CH_2$	$CH_3.CH_2.CHO$	$CH_2 = CH.CHO$
180	602	0.004	0.016	0.011	0.032
*180	604	0.001	0.024	0.012	0.032
*360	604	0.0016	0.022	0.012	0.034

* Indicates runs with reduced light intensity

From the results, it can be said that reducing the light intensity has little effect on the quantum yields of the products. There is some increase in the ϕ for 2-epoxy propane, whereas there seems to be a decrease in the ϕ for acetaldehyde, but this may be due to the difficulty in measuring the peak area of the acetaldehyde peak.

4.7 EFFECT OF ADDED NITROUS OXIDE

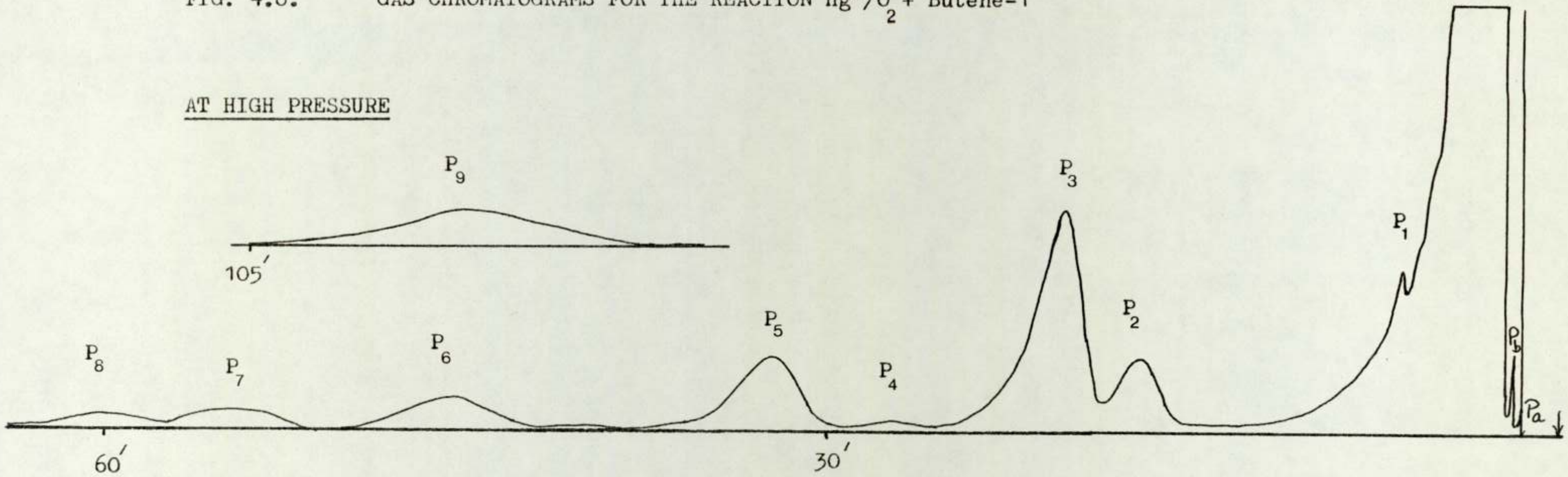
To study the effect of nitrous oxide added on the quantum yields of products, two separate runs were carried out in a similar way as has been explained in section 3.11. The results are summarized in Table 4.7 as under.

Irradiation time (min.)	Pressure (mm)	Quantum Yields				
		CH_3CHO	$CH_3CH\underset{O}{—}CH_2$	$CH_3.CH_2.CHO$	$CH_2=CH\cdot CHO$	$CH_2=C(CH_3).CHO$
180	586	0.005	0.004	0.0116	0.028	0.007
210*	550	0.0045	0.073	0.13	0.022	0.006
300	101	0.020	0.023	0.0056	0.046	0.0088
310*	98	0.023	0.035	0.010	0.042	0.0091

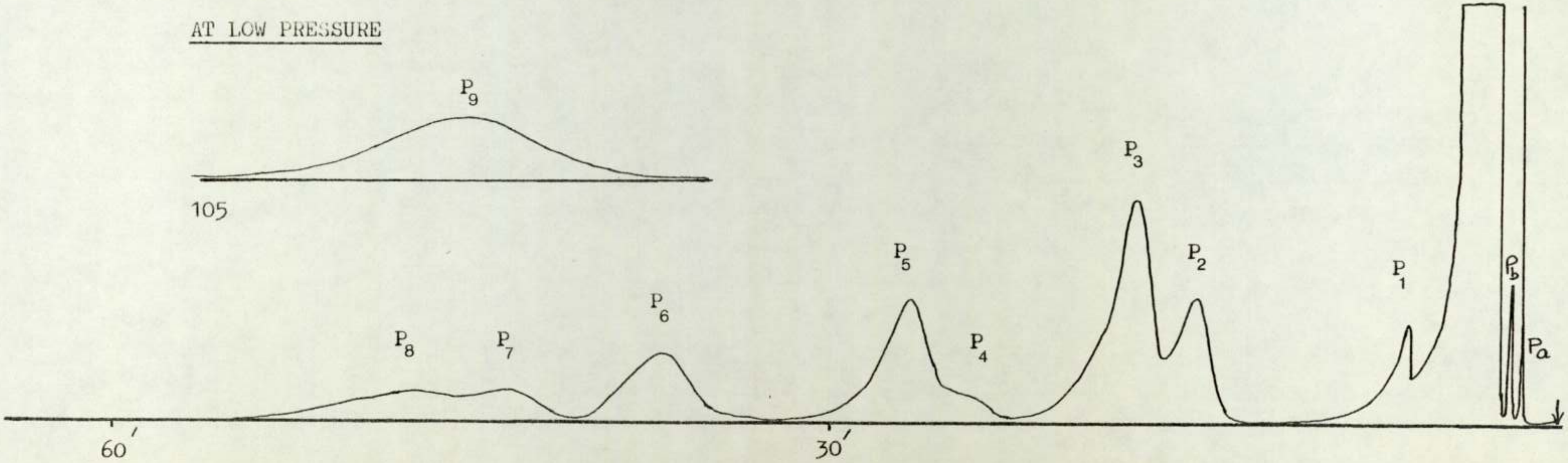
The results show that irradiation in the presence of nitrous oxide brings about changes in the quantum yield of some products. The yield of epoxide and propanal shows a pronounced increase whereas there is very little effect on the yields of the remaining products.

FIG. 4.8. GAS CHROMATOGRAMS FOR THE REACTION Hg^{*}/O_2 + Butene-1

AT HIGH PRESSURE



AT LOW PRESSURE



4.8 CHROMATOGRAMS FOR BUTENE-1

The chromatograms at both high and low pressures for the reaction of Butene-1 with Hg^*/O_2 is presented in fig. 4.8. The irradiation time during a normal run was five hours. All studies were made at room temperature 18 ± 3°C and the column used during the study was a 4 meter di-n butylphthalate with 2% Carbowax.

Gas pressures for the GLC were:

P_{N_2} (carrier gas) $\longrightarrow$ 30 lbs/in^2

P_{H_2} $\longrightarrow$ 28 lbs/in^2

P_{Air} $\longrightarrow$ 30 lbs/in^2

The symbols used in the chromatograms for the products are explained below.

P_1	represents	the	product	unidentified
P_2	"	"	"	"
P_3	"	"	"	Propanal
P_4	"	"	"	unidentified
P_5	"	"	"	α-Butene-oxide
P_6	"	"	"	n-Butanal
P_7	"	"	"	2-Butanone
P_8	"	"	"	unidentified
P_9	"	"	"	"

P_a and P_b were also two unidentified products eluding before the main alkene peak.

4.9 IDENTIFICATION OF PRODUCTS

The products from the reaction of butene-1 and Hg^*/O_2 were not separated and isolated from the glc and hence could not be identified by the mass spect. and I.R. techniques. They were however identified by their retention times and by the introduction of known samples in the glc.

Brief notes are provided below for each of the products identified.

(P_3) Propanal

Propanal was a major product. It was found to have the same retention time as that of a pure sample of it on the 4 m. di-n-butylphthalate column. Its peak increased in size when a pure sample of it was mixed ($<$ 1 mm.) with the reaction mixture and a sample introduced into the glc. It was thought that the confirmation was sufficient.

(P_5) α-Butene oxide

The epoxide was also a major product. Its peak also increased when a pure sample of it was introduced in the reaction system, mixed and the sample introduced onto the glc, furthermore its retention time matched with that of a pure sample of it on the di-n-butylphthalate column.

(P_6) n-Butanal

This compound was also confirmed by comparing its retention time with that of a pure sample of it on the di-butylphthalate column. The matching was unambiguous. It was also identified by the introduction of its pure sample in the reaction mixture and observing the peak size which increased.

(P_7) 2-Butanone

This compound was identified by comparing its retention time with that of a pure sample of 2-butanone on di-n-butylphthalate column. It was found that the matching was quite unambiguous. Its peak also increased when a small amount ($<$ 1 mm.) of its authentic sample was introduced in the reaction mixture and a sample taken for analysis in the glc.

The remaining products could not be identified due to the shortage of time as it would have required the proper separation and collection for the I.R. and mass spect. techniques. Hence the further studies on the reaction of Butene-1 and Hg^*/O_2 had to be abandoned.

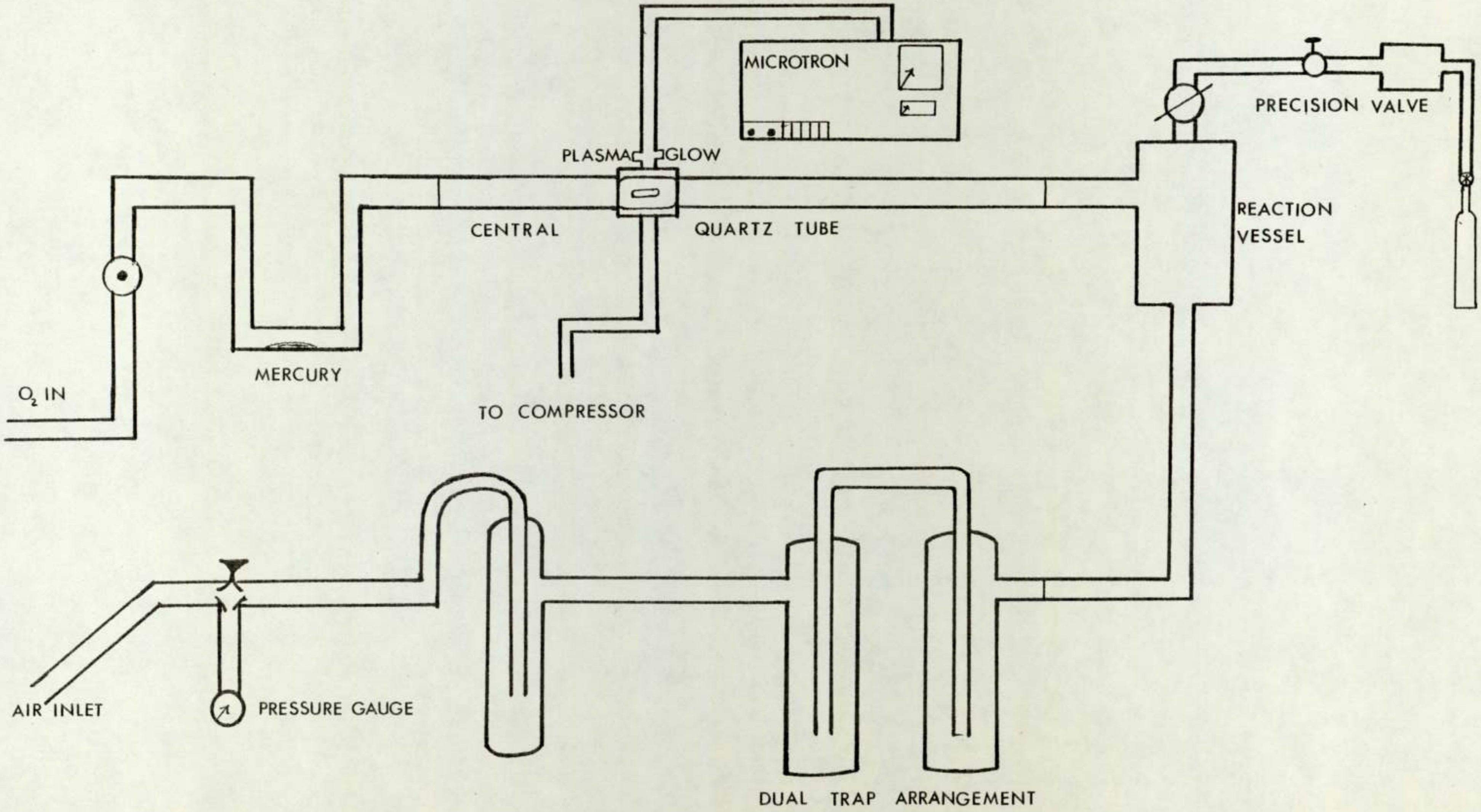
4.10 TESTS FOR HYDROPEROXIDES

During a normal run the test for the detection of any peroxides or hydroperoxides present was performed. The method is described elsewhere.

It was found that there was no colour development during independent runs with the propene and Butene-1. The test was repeated but again it gave a negative result. It was anticipated therefore that either the peroxides are not formed in the system (under study) or they decompose very soon to give stable products during the course of analysis prior to their detection.

FIG. 5.1

MICROWAVE DISCHARGE SYSTEM



CHAPTER FIVE

RESULTS OF THE REACTION OF SINGLET MOLECULAR OXYGEN (FROM MICROWAVE DISCHARGE) WITH ALKENES

5.1 THE MICROWAVE DISCHARGE SYSTEM

The microwave apparatus consisted of a simple vacuum line built on a metal frame. The central part of the line consisted of a long quartz tube which passed through a microwave cavity (as shown in the fig. 5.1).

The microwave power is obtained at 2450 MHz. at up to 200 watts continuous wave by a microwave generator Microtron 200 mark III made by Electro Medical Supplies Ltd. It is designed to operate from a mains supply of alternating current with a frequency of between 40 and 60 Hertz. The normal method of initiating the discharge is by means of a spark from a Tesla coil.

A Springham greaseless tap is attached between the oxygen supply and the narrow tubing (inside a bottle with some silicone oil) to control the pressure of molecular oxygen and to maintain uniform bubbling. A U-tube containing liquid mercury is situated before the plasma glow so that the line is saturated with mercury vapour. The central region of the quartz tube is cooled by air from a compressor.

The quartz tube is connected to the constructed pyrex glass reaction vessel (as shown in fig.) by means of a B_{14} socket. The other side of the reaction vessel is connected to a dual trap arrangement (in a dewar of liquid nitrogen) used for trapping and condensing the products.

Reactant gases are passed directly from a cylinder through a precision valve arrangement into the reaction vessel.

The dual trap arrangement is connected to a cold trap which in turn is connected to an Edwards vacuum pump through a three way greased tap which marks the end of the vacuum line. The pressure was usually kept between five and six torr.

Although relatively large concentrations of $O_2(^1\Delta g)$ can be produced by the discharge in a low pressure oxygen flow system, atomic oxygen is also a product (typically a few percent of both O and $O_2{}^1Og$ are formed). Atomic oxygen reacts with molecular oxygen to form ozone.(217)

$$O + O_2 + M \longrightarrow O_3 + M$$

Mercury vapour is present in the system and effectively removes oxygen atoms.

5.2 EXPERIMENTAL PROCEDURE

During a run firstly the microwave generator is on and left for warming up. The diffusion pump is also started and the whole system is open to the pumps for evacuation. When the whole system is evacuated, then oxygen is allowed in the system via the narrow capillary tubing. The flow rate can be controlled by means of the greaseless tap when the pressure in the system reaches between five and six torr, as shown on the pressure gauge, then the discharge is initiated by means of a Tesla coil. At this stage compressor is also switched on. Initially the power on the Microtron was varied from 30 to 50 watts and finally up to 70 watts.

The alkene to be reacted is then slowly passed through the inlet of the reaction vessel, where it can react with the excited molecular oxygen produced from the discharge. Any products formed are condensed in the dual trap arrangement along with the unreacted alkene. The reaction was continued usually for the time required (from thirty to sixty minutes in the present study). Pressure is checked from time to time to ensure that there are no leaks in the system.

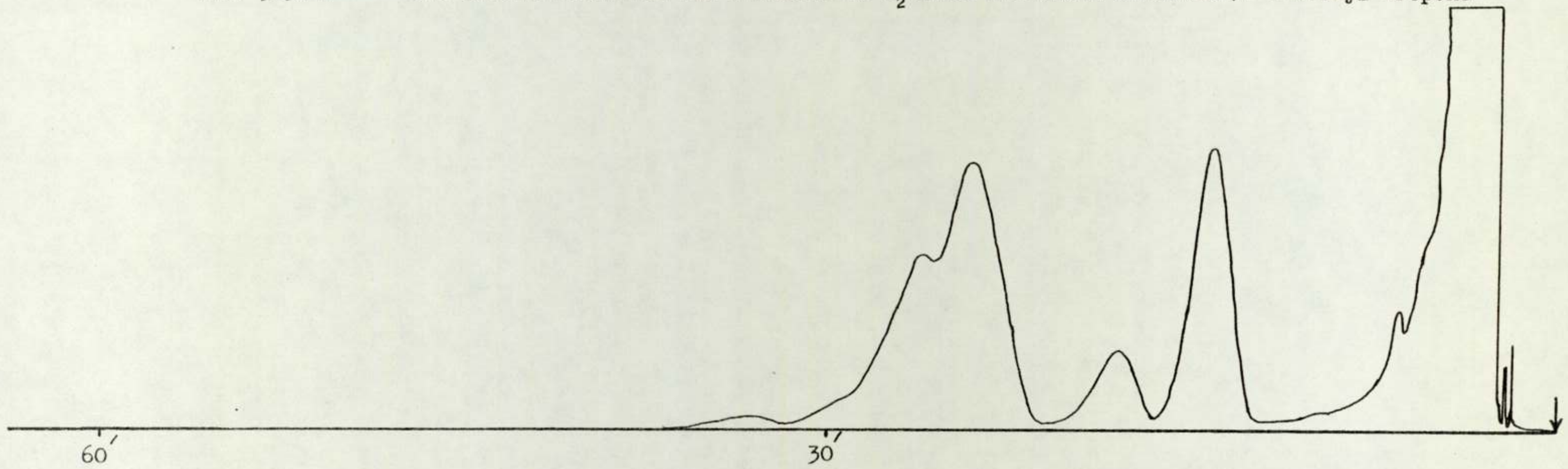
After the required reaction time completed the flow of the alkene was stopped and the reaction vessel was closed. The microtron was shut off and the oxygen flow was also stopped. The greased taps on the dual trap arrangement were closed and it was very carefully removed from the rest of the apparatus, still immersed in the liquid nitrogen. It was then subjected to the evacuation by means of attaching it to the manifold of the main apparatus (described in Chapter 2). It was degassed twice, and was then transferred into the reaction system by allowing it to warm up very slowly and carefully by means of a dryer. After all of the reaction mixture was transferred, its total pressure was noted and it was circulated for at least forty minutes to ensure thorough mixing before introducing the first sample for analysis into the glc.

5.3 RESULTS WITH 2-METHYL PROPENE, PROPENE AND BUTENE-1

After the results of mercury photosensitized oxidations with 2-methyl propene were almost complete, it was thought necessary to work on the microwave discharge system so that a comparison could be made between the singlet oxygen + alkene products and Hg^*/O_2 + alkene products whether there are any similarities between the two reactions, and whether the singlet oxygen is involved in the Hg^*/O_2 system.

During a typical run, a continuous flow of 2-methyl propene was kept through the reaction vessel for 45 minutes during which some bluish green coloured mass was observed in the trap. The trap was then carefully removed from the discharge system and was attached to the main apparatus for degassing. After degassing twice, it was

FIG. 5.3.1. GAS CHROMATOGRAM FOR THE REACTION OF $^1O_2$ (FROM MICROWAVE DISCHARGE)+ 2-Methyl Propene



GAS CHROMATOGRAM FOR THE REACTION Hg^*/O_2 + 2-Methyl Propene AT LOW PRESSURE

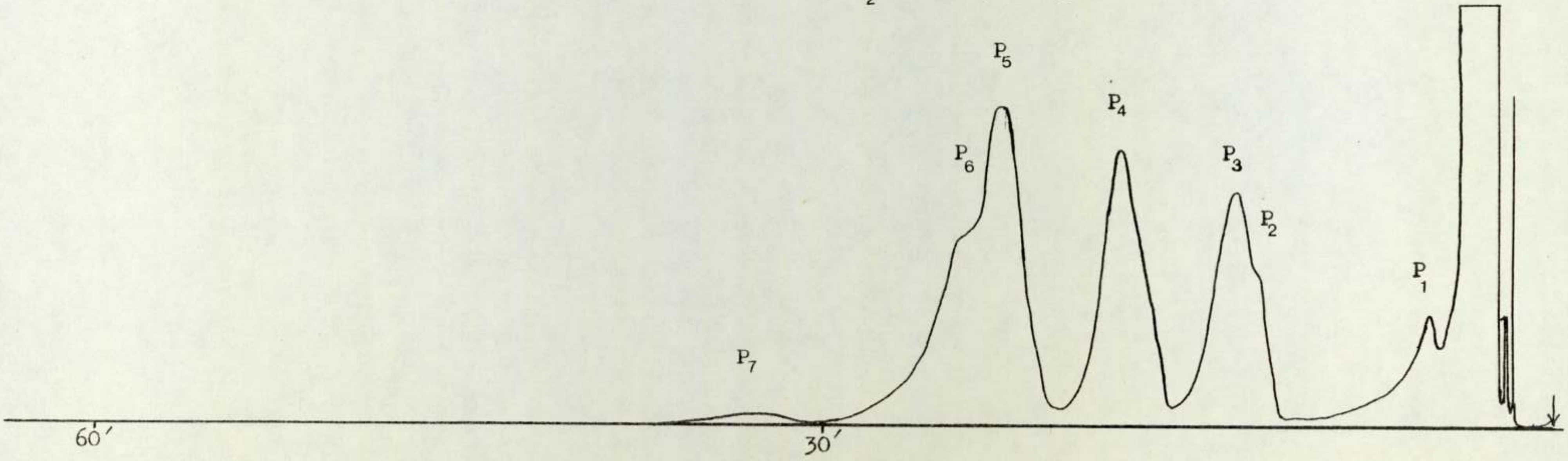
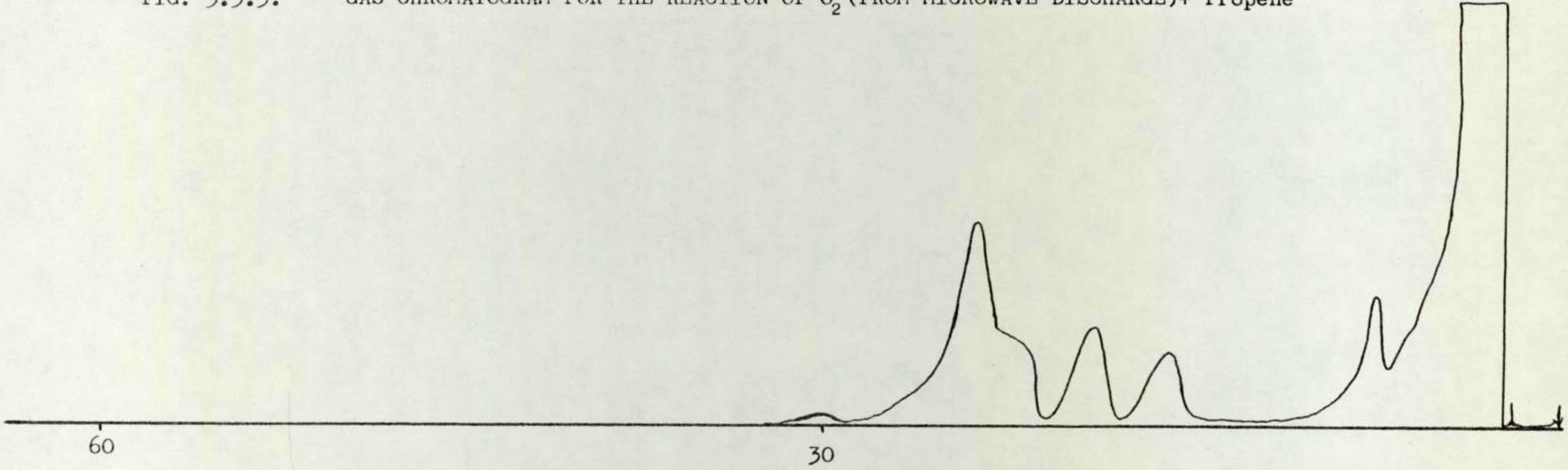


FIG. 5.3.3. GAS CHROMATOGRAM FOR THE REACTION OF $^1O_2$ (FROM MICROWAVE DISCHARGE)+ Propene



GAS CHROMATOGRAM FOR THE REACTION Hg^*/O_2 + Propene AT LOW PRESSURE

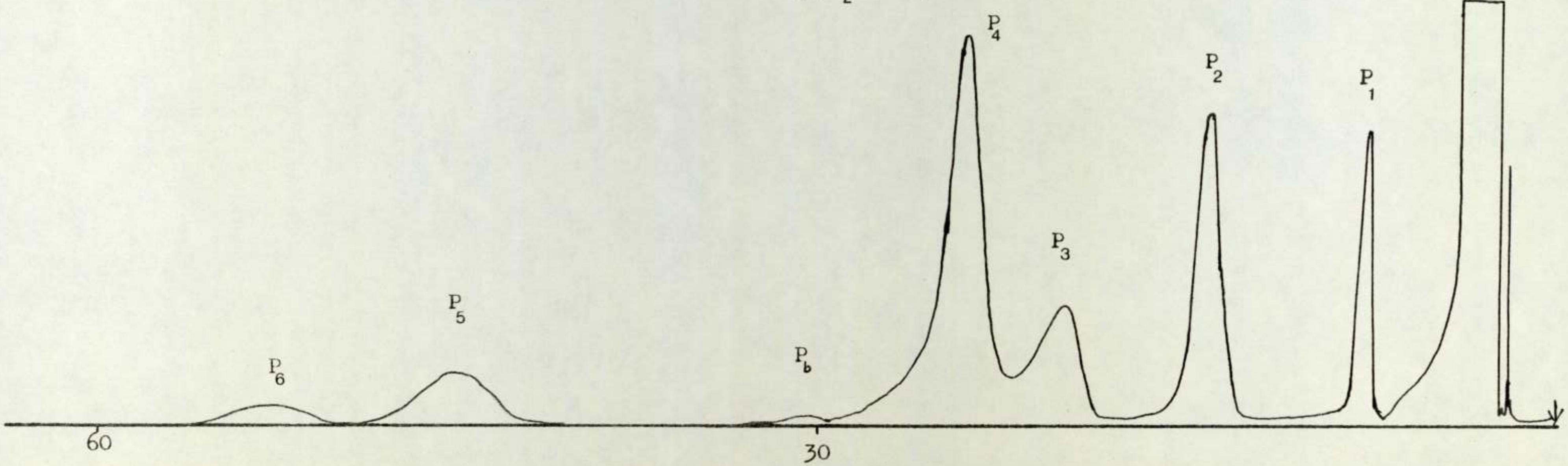
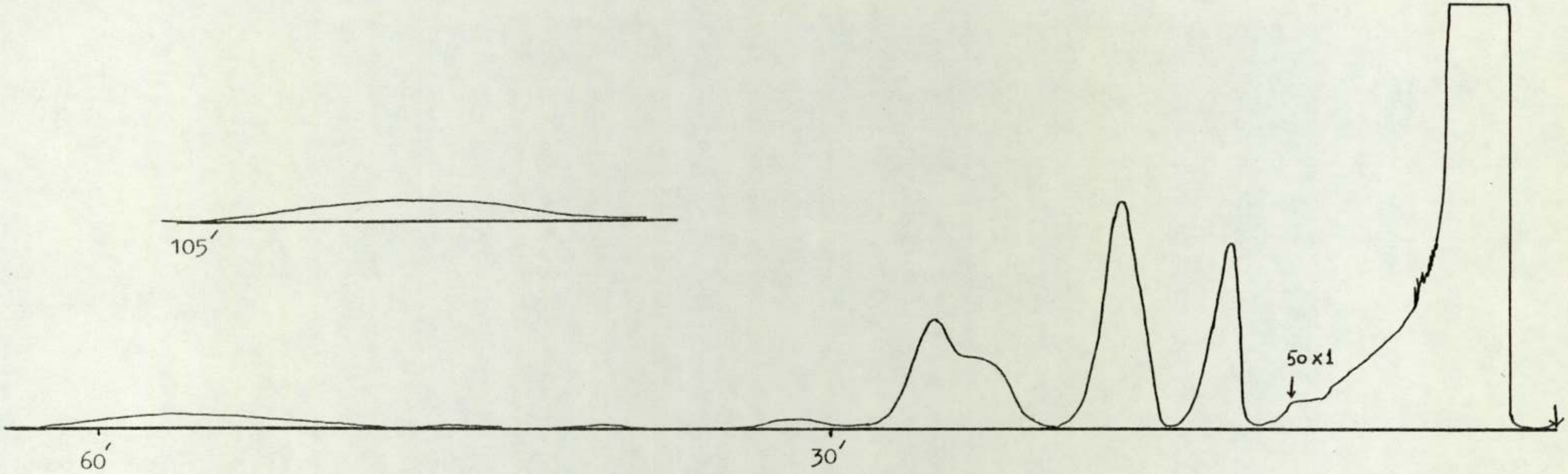


FIG. 5.3.4. GAS CHROMATOGRAM FOR THE REACTION OF $^1O_2$ (FROM MICROWAVE DISCHARGE)+ Butene-1



GAS CHROMATOGRAM FOR THE REACTION Hg^*/O_2 + Butene-1 AT LOW PRESSURE

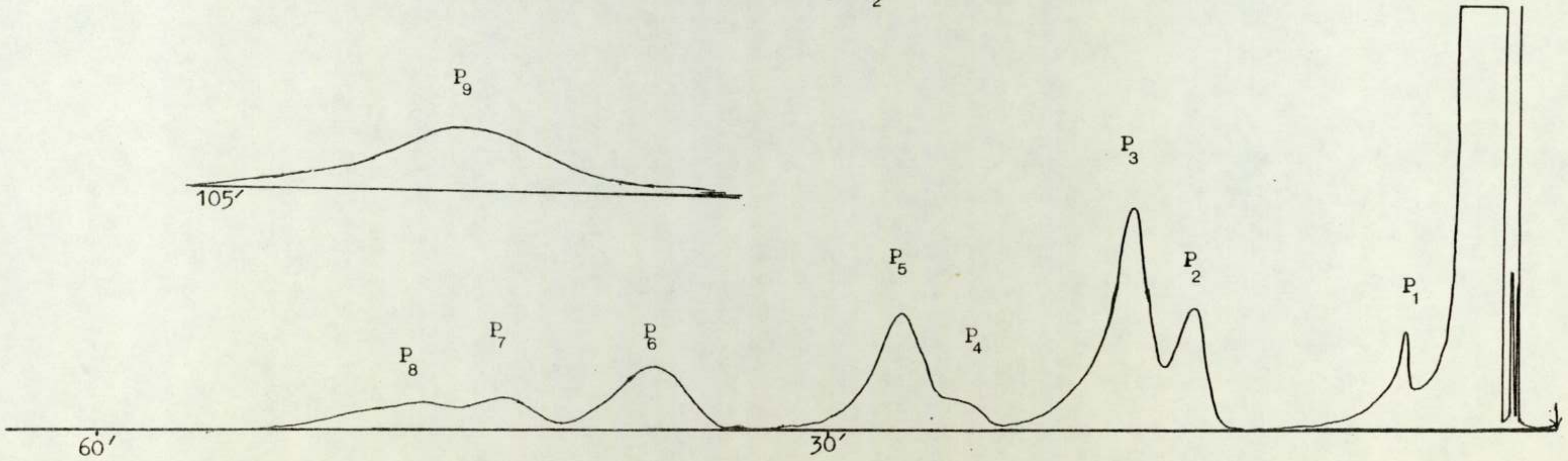


FIG. 5.3.2. GAS CHROMATOGRAM FOR THE REACTION OF $^1O_2$ (FROM MICROWAVE DISCHARGE) + 2-Methyl Propene

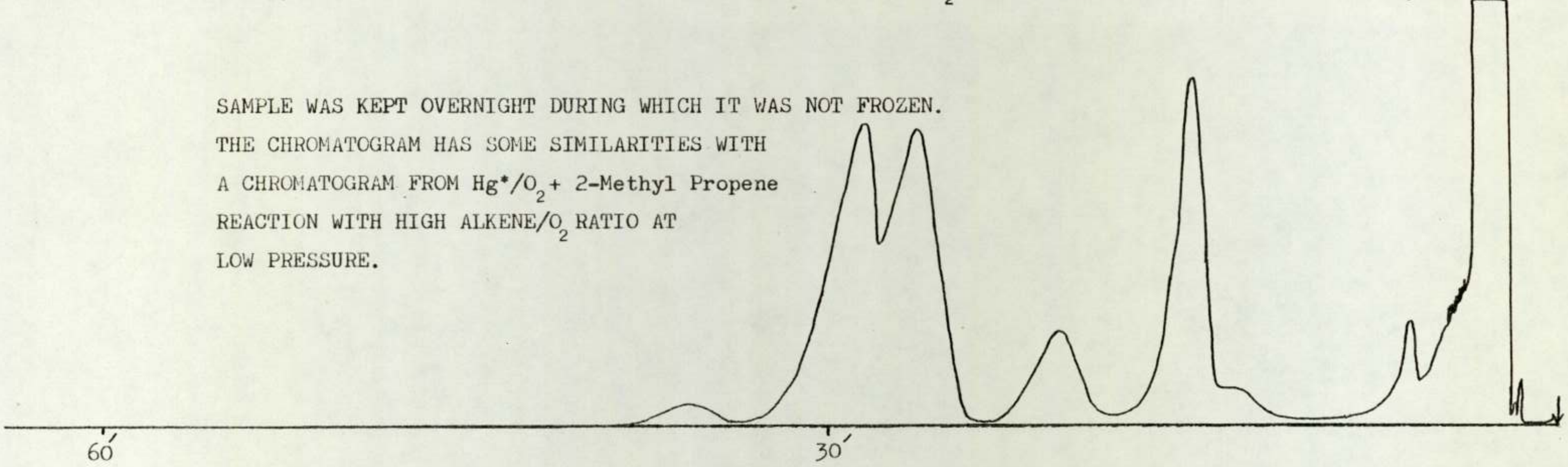
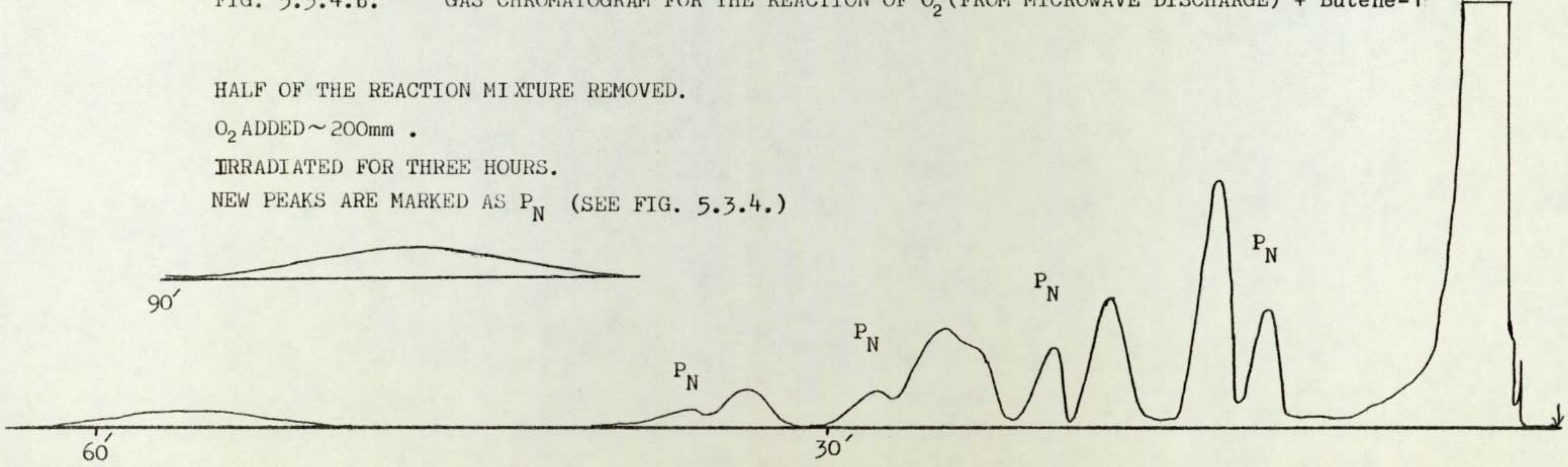

SAMPLE WAS KEPT OVERNIGHT DURING WHICH IT WAS NOT FROZEN.
THE CHROMATOGRAM HAS SOME SIMILARITIES WITH
A CHROMATOGRAM FROM Hg^*/O_2 + 2-Methyl Propene
REACTION WITH HIGH ALKENE/O_2 RATIO AT
LOW PRESSURE.

FIG. 5.3.4.b. GAS CHROMATOGRAM FOR THE REACTION OF $^1O_2$ (FROM MICROWAVE DISCHARGE) + Butene-1


HALF OF THE REACTION MIXTURE REMOVED.
O_2 ADDED ~ 200mm .
IRRADIATED FOR THREE HOURS.
NEW PEAKS ARE MARKED AS P_N (SEE FIG. 5.3.4.)

allowed to warm up slowly and was transferred to the reaction system. At this stage the test for any peroxides present was performed, as explained in section 3.4. It was then subjected to glc analysis. The glc conditions were same as those in the Hg^*/O_2 reaction. The results of the chromatogram are provided in fig. 5.3.1. One sample was injected onto the glc after keeping it overnight during which the reaction mixture was not frozen. Its results are provided in fig. 5.3.2.

It can be seen from the results of the chromatograms which are compared against a chromatogram of a normal run with Hg^*/O_2 and 2-methyl propene that there are some similarities between the nature of products from the two reactions.

It was not possible unfortunately due to shortage of time to make a detailed identification of the products from the microwave experiments, as there were problems involved in the collection. It is difficult to say about the nature of products by means of retention times on one column only without making use of the other identification techniques.

It was found that there was no product formation when 2-methyl propene was subjected to pass through the discharge in place of oxygen and molecular oxygen was introduced through the reaction vessel.

A comparison of products from the reaction of excited singlet oxygen from microwave + propene and Hg^*/O_2 + propene is provided in the chromatograms from the glc analysis shown in fig. 5.3.3. It can be said that there are few similarities between the products of the two reactions.

In the case of Butene-1 the results of the reaction are again compared with the Hg^*/O_2 + Butene-1 reaction and it can be seen from the chromatograms shown in the fig. 5.3.4. that there are little similarities between the products of the above two reactions. During the butene-1 run, after two or three readings for the glc were taken, about half of the reaction mixture was pumped away and molecular oxygen (about 200 mm.) was introduced in the system. After a thorough mixing, the whole reaction mixture (about 550 mm.) was irradiated for three hours, the aim was to see the common products of the two reactions, because products whose peak increased after the irradiation would be likely to be similar. It was found that there were little similarities as some product peaks increased in size whereas some new peaks were formed, indicating the non-similar products.

Hence from the results quoted above, it can be said that there are some similarities in the case of singlet oxygen from microwave discharge + 2-methyl propene and Hg^*/O_2 + 2-methyl propene reaction and similarly with propene and butene-1 again there are some similarities. It seems fair to assume then that singlet molecular oxygen probably takes some part in the Hg^*/O_2 system and perhaps it is responsible for the formation of some products in the Hg^*/O_2 reaction of 2-methyl propene, propene and butene-1.

CHAPTER SIX

DISCUSSION OF THE MERCURY PHOTOSENSITIZED OXIDATION OF 2-METHYL PROPENE

Firstly in this chapter the nature of the products formed from the mercury photosensitized oxidation of 2-methyl propene with molecular oxygen will be discussed. An attempt will be made to suggest plausible origins of the observed products and to account reasonably well for the observed dependencies on the reaction parameters.

6.1 PRIMARY PROCESSES

As already mentioned in the introduction, the following processes should be considered as important in any Hg^*/O_2/alkene system.

$$Hg6^1S_0 + h\nu 253.7 \text{ n.m} \longrightarrow Hg6^3P_1 \text{ ——— } (1)$$

The excited mercury atom may be quenched by either the oxygen or the alkene.

$$\begin{tikzcd} Hg6^3P_1 + O_2\,{}^3\Sigma_g^- \arrow[r] & Hg6^1S_0 + O_2\,({}^1\Sigma_u^-) \arrow[dl] \arrow[dr] & \text{——— } (2) \\ O_2\,{}^1\Delta g & & O_2\,{}^1\Sigma g^+ \end{tikzcd}$$

The formation of either ${}^1\Sigma_u^-$ or ${}^3\Delta u$ of which the former is more probable can result in the rapid formation of ${}^1\Delta\, gO_2$ in a high vibrational level.(187)

$$Hg6^3P_1 + {>}C = C{<} \longrightarrow Hg6^1S_0 + ({>}C = C{<})^* \text{ ——— } (3)$$

where $({>}C = C{<})^*$ is an electronically excited alkene molecule.

In the Hg^*/O_2 system the reaction

$$Hg6^3P_1 + O_2\,{}^3\Sigma g^- \longrightarrow (Hg.O_2)^* \text{ ——— } (4)$$

is also a possibility.(197)

It has been suggested that the quenching cross section for the above reaction (reaction 4) is .025(n.m)^2,(197) whereas for reaction

(2) it is $1.99(\mathrm{nm})^2$ (9, 11) and for reaction (3) it is $5.3(\mathrm{nm})^2$.(5) It would seem therefore that the reactions (2) and (3) will dominate over reaction (4). During most runs the ratio of oxygen to alkene was more than 10 : 1, hence it is anticipated that most of the excited mercury will be quenched by oxygen under those conditions.

Ozone and oxygen atoms are known products of Hg^*/O_2 system and the following reactions may be important involving the excited oxygen molecule.

$$O^*_2 + O_2 \longrightarrow O_3 + O \tag{5}$$

$$O^*_2 + O_2 \longrightarrow O_2 + O_2 \tag{6}$$

$$O + O_2 + M \longrightarrow O_3 + M \tag{7}$$

$$(Hg.O_2)^* + O_2 \longrightarrow HgO + O_3 \tag{8}$$

$$O^*_2 + (>C = C<) \longrightarrow (>C = C<)^* + O_2 \tag{9}$$

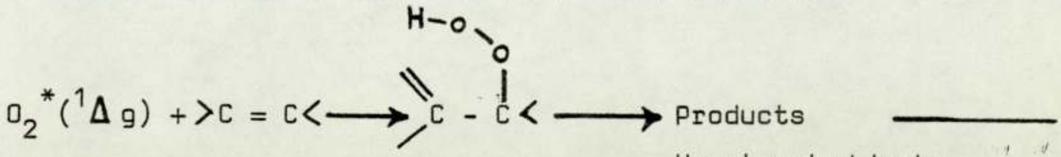
Reactions 1 - 4 and 5 - 9 can account for the necessary reactive species needed to give the observed products from 2-methyl propene and the intermediates in the reaction.

In the reaction (9), O^*_2 transfers its energy to the alkene and $(>C = C<)^*$ is an excited alkene molecule whose energy is supposed to be less than the excited alkene molecule in reaction (3). Heicklen(205) has suggested this energy transfer reaction, while dealing with mercury photosensitized oxidation of per fluoro alkenes.

The quantum yield of ozone for reactions (5) and (7) has been said to lie in the range of 0.03(183) to 0.14(184), where as the quantum yield of ozone for the reaction (8) has been interpreted as 0.5(194).

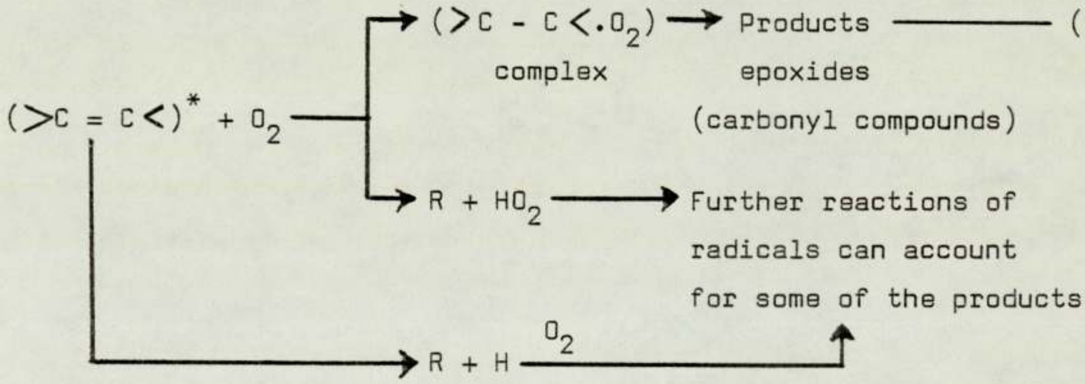
6.2 REACTIONS OF POSSIBLE REACTIVE SPECIES WITH THE ALKENES

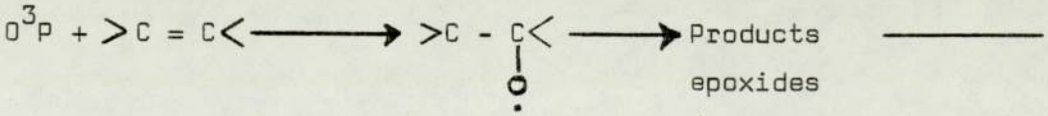
In the presence of an alkene (here 2-methyl propene), the excited oxygen and the products formed by the reactions indicated by equations (5), (7), (8) and (9) will react rapidly with the alkene presumably by the following main processes.



$$O_2^{*}(^{1}\Delta g) + {>}C = C{<} \longrightarrow {=}C - \overset{\overset{H-O-O}{|}}{C}{<} \longrightarrow \text{Products} \qquad (10)$$

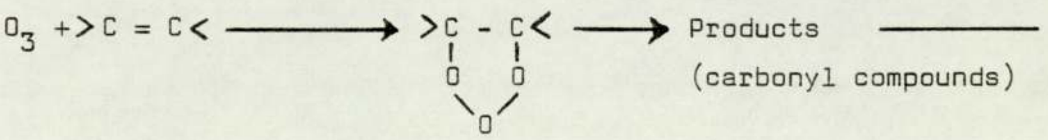
Unsaturated hydroperoxides, carbonyl compounds, alcohols etc.





$$O^{3}P + {>}C = C{<} \longrightarrow {>}C - \underset{\underset{O\cdot}{|}}{C}{<} \longrightarrow \text{Products} \qquad (12)$$

epoxides
(carbonyl compounds)

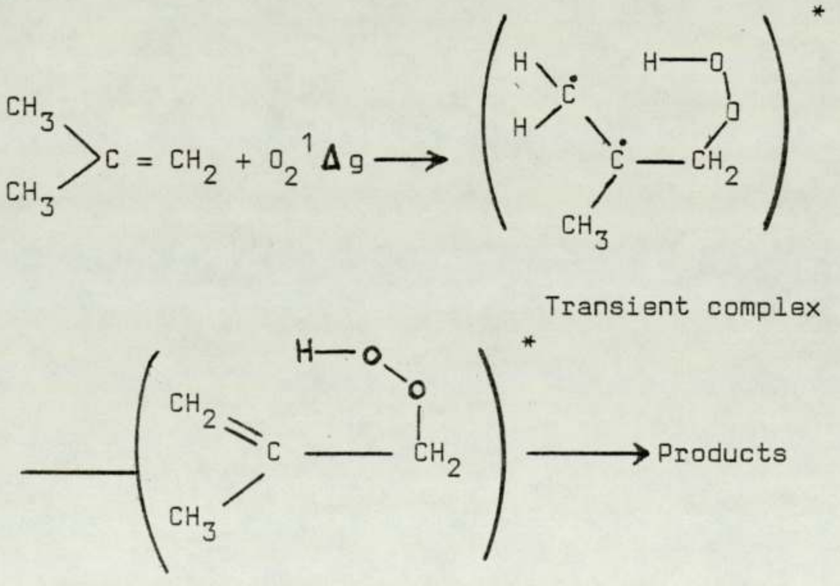


$$O_3 + {>}C = C{<} \longrightarrow {>}\underset{\underset{O}{|}}{C} - \underset{\underset{O}{|}}{C}{<} \longrightarrow \text{Products} \qquad (13)$$

(carbonyl compounds)

To consider the overall mechanism of the mercury photosensitized oxidation of alkenes one has to consider each of the above processes 10 - 13 in at least some detail since they all amongst them can account for the product formation and their dependence on various parameters.

Reaction (10) proceeds through the addition of excited oxygen in the $^1\Delta g$ state, which results in the formation of a hydroperoxide. In most reactions of singlet oxygen molecules with alkenes the major oxidation products are rearranged allylic hydroperoxides$^{(71, 75, 99)}$. The double bond always shifts and the reaction is most favourable when the hydrogen which is removed can be coplaner with the pi lobes of the double bond. These hydroperoxides are thermally unstable and sensitive to surface catalysis, hence their decomposition may lead to aldehydes and alcohols observed in the products with double bond still present.$^{(75)}$ The reaction of $O_2{}^1\Delta g$ with 2-methyl propene in the system would be as follows.



Reaction (11) proceeds through the reaction of excited alkene molecule with O_2. It can either form a complex with O_2 which can then proceed to give the products as shown below.

$$(>C = C<)^* + O_2 \longrightarrow \underset{\text{Hot complex}}{(>C = C < .O_2)^*}$$

According to Heicklen$^{(205)}$ the complex might do any of the following:

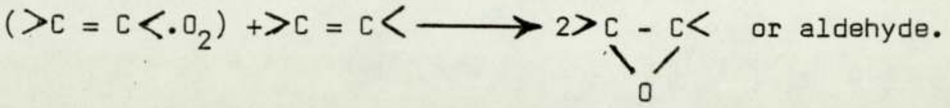
$$(>C = C<.O_2) \longrightarrow RO_2 + R$$

$$\longrightarrow R.CHO + H.CHO$$

$$\longrightarrow \text{Aldehyde} + O$$

$$\longrightarrow \text{epoxide} + O$$

or it may experience a collision with another alkene molecule to give the product



$$(>C = C<.O_2) + >C = C< \longrightarrow 2>\underset{\diagdown O \diagup}{C - C}< \quad \text{or aldehyde.}$$

Instead of forming the complex with O_2 it is possible that radicals are produced.$^{(208)}$

$$(>C = C<)^* + O_2 \longrightarrow R. + HO_2$$

$$R + O_2 \longrightarrow RO_2$$

$$RO_2 + >C = C< \longrightarrow ROOH + R$$

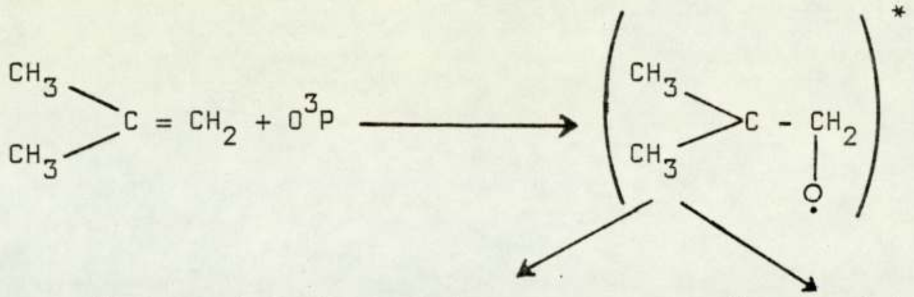
$$RO_2 + HO_2 \longrightarrow ROOH + O_2$$

$$RO_2 + RO_2 \longrightarrow 2\ RO. + O_2$$

$$RO + RH \longrightarrow ROH + R$$

These and the further reactions could account for the formation of aldehydes, alcohols and some minor products.

Reaction (12) proceeds through the reaction of oxygen atoms O^3P with alkenes. This reaction has been well described in the introduction. Cvetanovic$^{(15)}$ has proposed the initial adduct as a biradical with oxygen attached preferably to the less substituted carbon atom of the double bond. The reaction proceeds with predominant fragmentation in the case of small alkenes because the excess energy of the biradical cannot be removed easily by collisions, and appears to be supressed in the case of more complex alkenes. In the system under study, the reaction would follow as



(Mainly at P > 50 mm Hg)

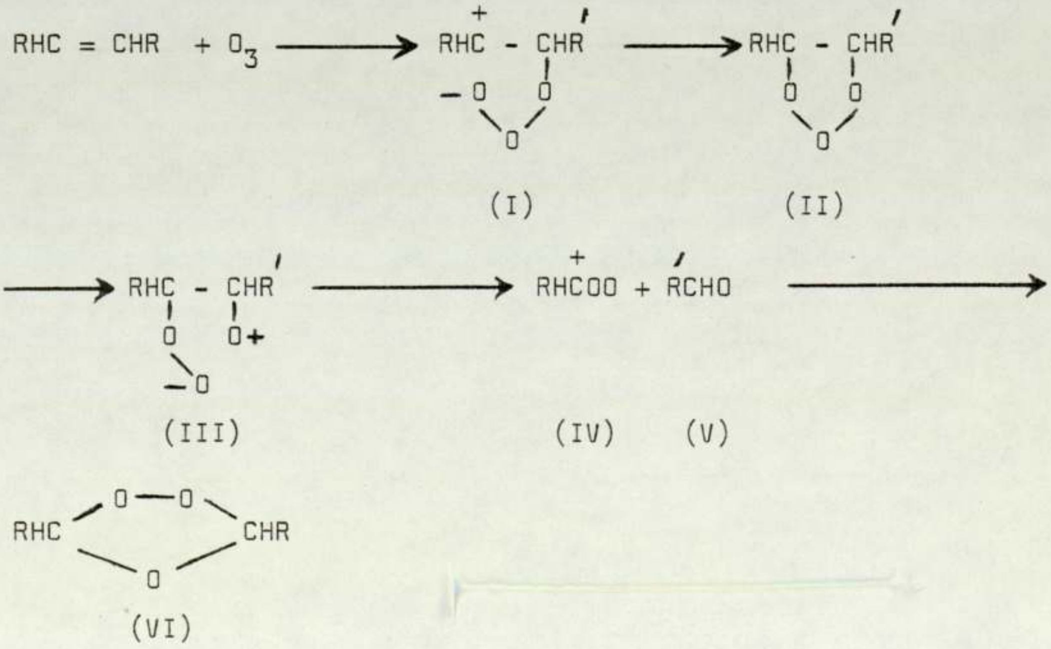
Epoxides and Aldehydes

(Fragmentation)

Aldehydes, ketones with smaller no. of carbon atoms plus lower members of hydrocarbon.

The ratio epoxide to aldehyde is approximately equal to 0·95 ⟷ 1·17.(55)

Reaction (13) proceeds through the ozonolysis of the alkene. Ozone reactions are of great complexity and have received little attention. Cvetanovic and Vrbaski have carried out the reactions of ozone with a number of alkenes in the gas phase.(213) They have explained the product formation in terms of the following generally accepted mechanism of ozone interaction with alkenic compounds.



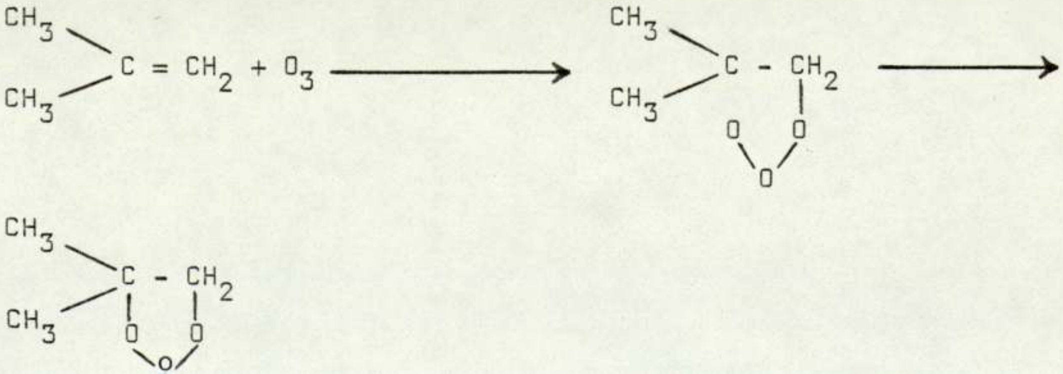
The initial addition may be a two step process as indicated by the above scheme in which (I) could be visualized as a π -complex.(214)

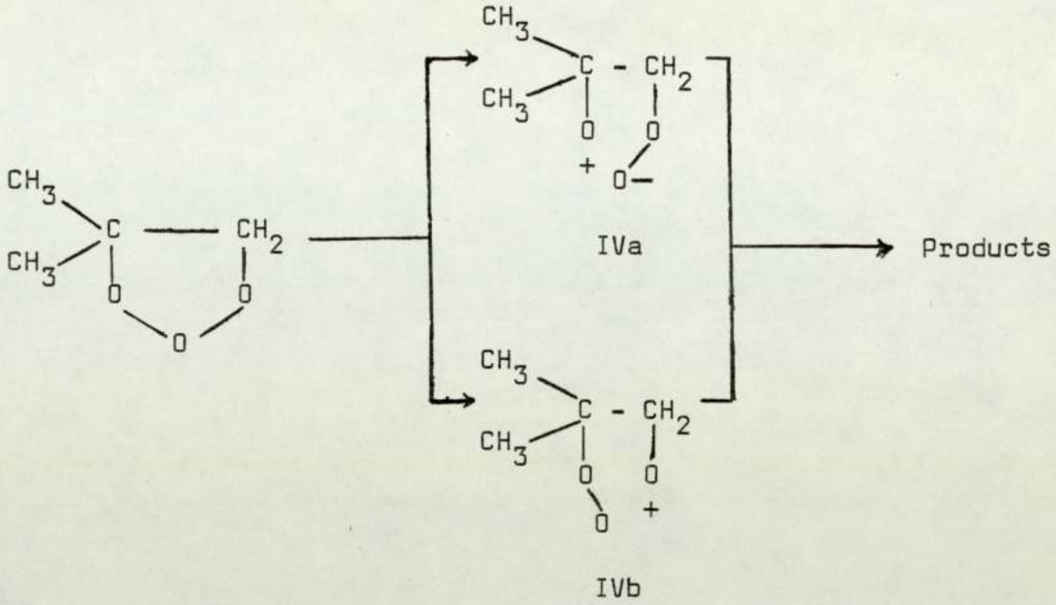
A one step addition would otherwise lead directly to the initial ozonide (II) which is very unstable. Criegee(215) has obtained evidence that the initial ozonide is formed at least under some conditions. He and his co-workers identified (IV) as a relatively stable and long lived zwitterion which on addition to an aldehyde (V) forms an ozonide (VI). At high temperatures and in the vapour phase other competing reactions of the zwitterion become important and the process is quite complex. These zwitterions can undergo many types of reactions such as dimerization, polymerization with or without participation of water into peroxidic substances, rearrangement and decomposition. Cvetanovic and Vrbaski(213) during their study have said that there are in particular two features of the ozone reactions which are to be kept in mind.

(a) Appreciable quantities of relatively unstable intermediate peroxidic compounds are initially formed and the final stable products observed will depend on the conditions under which the degradation takes place. The particular analytical procedure used may therefore affect the amounts and the type of the stable product observed.

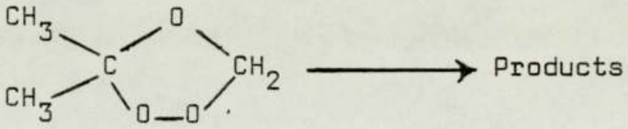
(b) The reactions are highly exothermic and the liberated heat is as a rule likely to affect their course at least to some extent, and sometimes quite markedly, mainly when a large excess of molecular oxygen is present.

In the present system, the mechanism of ozone addition to 2-methyl propene may be





The products from IVa and IVb may combine again to give the ozonide which can again decompose thermally to give stable products.



ozonide

The main products Cvetanovic and Vrbaski(213) obtained from their reaction of ozone and 2-methyl propene were acetone and formaldehyde. Rest of the products were 2-methyl propanal, methanol CO_2, propene, methyl formate, propane, methyl acetate and tertiary butanol. They have said that the peroxidic intermediates were formed in the system but decomposed during the course of glc analysis releasing the bound carbonyl compounds. The reaction was quite complex in nature.

The reactions 10 - 13 have been used to explain the products observed in the present system.

It would be necessary at this stage to mention about the results of the microwave experiments described in the previous chapter. It was found that there were some similarities in the case of 2-methyl propene + Hg^*/O_2 reaction and 2-methyl propene + $^1O_2^*$(from Microwave discharge) reaction. The observations will be utilized when discussing the formation of products.

The main products from the mercury photosensitized oxidation of 2-methyl propene with molecular oxygen are methacrylaldehyde, 2-methyl propanal, acetone and tertiary butanol. Minor products were propanal, acetaldehyde and 2-butanone.

Below are listed the principal observed products and their relative yields at different pressures and at different alkene/O_2 ratios.

TABLE 6.2.

Products	P_{Total} 600 mm.Hg		P_{Total} 100 mm.Hg	
	Yield at alkene/O_2 1 : 10	Yield at alkene/O_2 10 : 1	Yield at alkene/O_2 1 : 10	Yield at alkene/O_2 6 : 1
$CH_3.CH_2.CHO$	10	4	19	8
$CH_3.CO.CH_3$	80	43	170	100
$(CH_3)_2.CH.CHO$	85	16	120	30
$CH_2 = C(CH_3).CHO$	170	240	260	380
$(CH_3)_3C.OH$	19	40	30	140

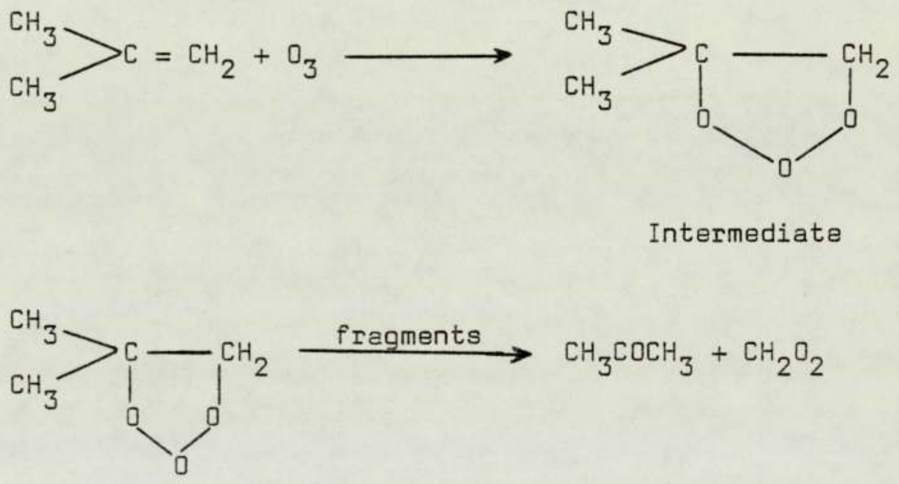
6.3 MAIN PRODUCTS AND MECHANISMS FOR THEIR FORMATION

The number of possible processes for the formation of major products are considerable. It is important to establish which of these processes are likely to be important in the overall reaction scheme. In the forthcoming notes, each of the major products is discussed with the satisfactory explanation for its formation and the dependancy on various parameters.

Acetone

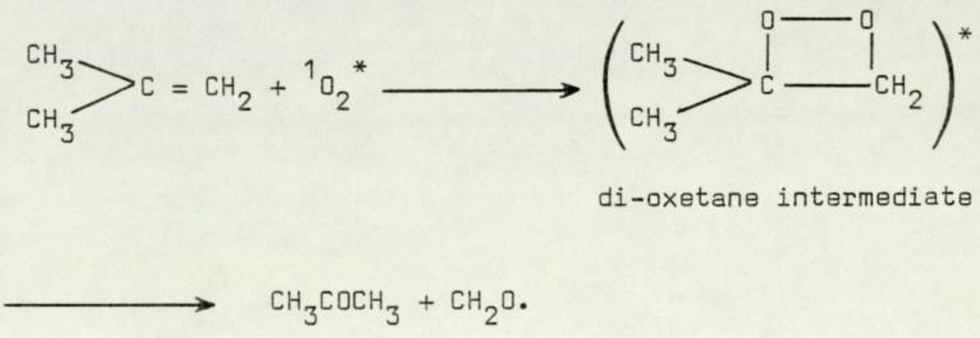
The possible routes for the formation of acetone are discussed below.

(a) From ozone

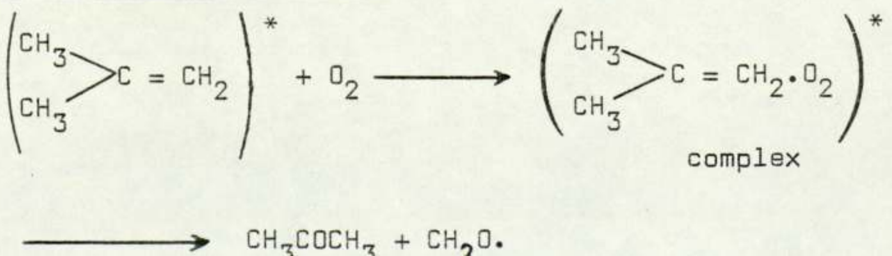


In the above case, the intermediate formed fragments by keeping the 2 atoms of oxygen with the less substituted carbon atom.

(b) From excited singlet oxygen



(c) From an excited alkene molecule



Of all the possible routes, only (a) is consistent with the observed results. Reaction (b) can be discounted on the grounds that although some of the earlier research indicated the possible occurence of such a process but there is sufficient evidence now that the dioxetane intermediates are less probable and may not be involved in the singlet oxygen reactions.(136 - 140) Reaction (c), though possible, cannot explain the decrease in the yield of acetone as the percentage of alkene is increased in the system. It seems that the formation of acetone is through ozone which explains the decrease in the yield at high alkene/O_2 ratio due to the increasing importance of the reaction

$$Hg6^3P_1 + \; >C = C< \longrightarrow Hg6^1S_0 + (>C = C<)^*$$

over

$$Hg6^3P_1 + O_2 \longrightarrow Hg6^1S_0 + O_2^*$$

During high alkene/O_2 ratio more mercury atoms will be quenched by the alkene and the higher rate of the reaction.

$$O_2^* + \; >C = C< \; \longrightarrow \text{Product}$$

will account for the low ozone yields by the reaction

$$O_2^* + O_2 \longrightarrow O_3 + O$$

This and the unimportance of further ozone producing reactions at high alkene/O_2 ratio

$$O + O_2 + M \longrightarrow O_3 + M$$

$$(Hg.O_2)^* + O_2 \longrightarrow HgO + O_3$$

could explain the reduction in acetone formation at high alkene/O_2 ratios.

The decrease in the yield during the high pressure runs in the pressure dependant studies can be explained by the deactivation process being important at high pressures

$$O_2^* + O_2 \longrightarrow O_2 + O_2$$

and the pressure stabilization of the hot intermediates.

In the previous studies of photo-oxidation of 2-methyl propene in the presence of molecular oxygen(216), significant amounts of acetone were recovered and also acetone is the major product of the reaction of ozone with 2-methyl propene in the vapour phase.(213)

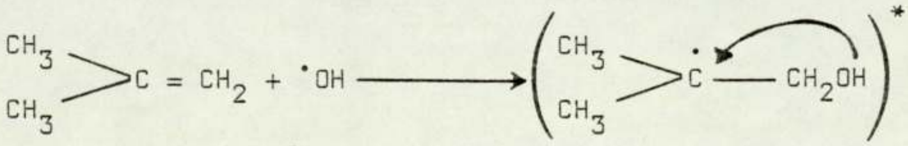
Considering the above explanations in the light of the results from the microwave experiments and the present Hg^*/O_2 system, it seems fair to assume that ozone is mainly responsible for the formation of acetone in the system under study.

2-Methyl Propanal

The presence of 2-methyl propanal among the products with the absence of isobutene oxide strongly suggested the non-participation of O^3P atoms in the 2-methyl propene/Hg^*/O_2 system. It shows the complex nature of the reaction which made speculation on its mechanism quite difficult.

The influence of other factors such as change of alkene/O_2 ratio, reducing the light intensity when its yield increased suggested that radical combination are not important for its formation. The possible reactions according to their importance are given below.

(a)



$$(CH_3)_2C{=}CH_2 + {}^{\bullet}OH \longrightarrow \left((CH_3)_2\dot{C}-CH_2OH\right)^*$$

hot intermediate

$$\longrightarrow (CH_3)_2\,CH.CHO + H^{\bullet} \qquad (\Delta H \approx -12KJ/_{mole})$$

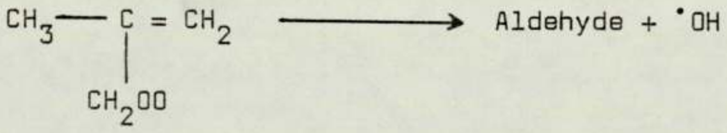
The $^{\bullet}$OH radicals may have been produced by the decomposition of the hydroperoxide

$$ROOH \longrightarrow RO^{\bullet} + {}^{\bullet}OH$$

Bell and McDowell(208) have suggested that in the hydrocarbon oxygen mixture reaction

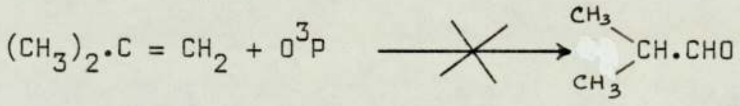
$$RH + O_2^{*} \longrightarrow RO\cdot + {}^{\bullet}OH$$

is also a possibility. The $^{\bullet}$OH radicals can also be formed by the decomposition of the methyl allyl peroxy radical formed by the addition of oxygen to the methyl allyl radical.



$$CH_3-\underset{\displaystyle CH_2OO}{\underset{|}{C}}=CH_2 \longrightarrow \text{Aldehyde} + {}^{\bullet}OH$$

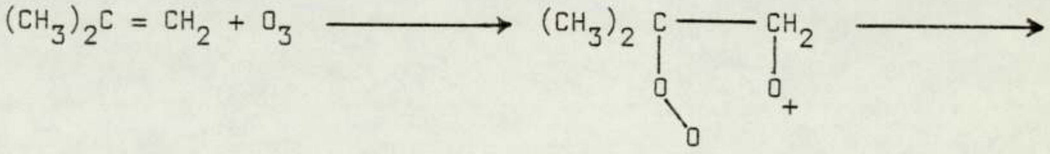
The above reaction seems to explain the formation of 2-methyl propanal in the system and reaction such as



$$(CH_3)_2.C = CH_2 + O^3P \not\longrightarrow (CH_3)_2CH.CHO$$

can be discarded for the reasons already given.

(b) The reaction through ozone may also contribute to some extent.



Intermediate

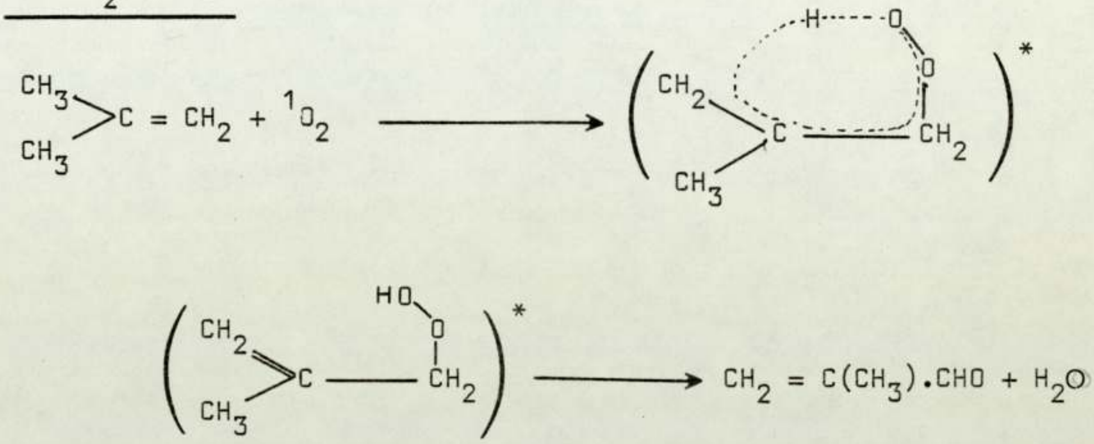
$$(CH_3)_2CH.CHO + O_2^{*}$$

Cvetanovic and Vrbaski have suggested that probably molecular oxygen splits off from the above intermediate and the remainder then rearranges to the aldehyde. The oxygen evolved may be in an excited singlet state.(96) However, the above reaction is relatively unimportant when compared with the reaction (a).

Methacrylaldehyde

The possible sources of methacrylaldehyde are as follows.

(a) From $O_2^*(^1\Delta g)$

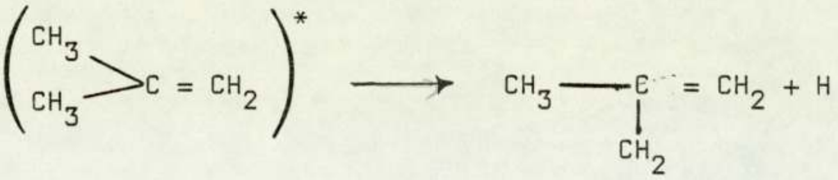


short lived hot molecule

In most reactions of singlet oxygen molecules with alkenes the major oxidation products are rearranged allylic hydroperoxides which may decompose to give carbonyl products. Probably in this case the methyl allyl hydroperoxide decomposes during the course of reaction giving the stable aldehyde detected in the system. Further the results of singlet molecular oxygen from microwave discharge with 2-methyl propene as described in the previous chapter (see fig. 5.3.1) show the peak on the GLC chromatogram in the same place having the same retention time as of methacrylaldehyde in the Hg^*/O_2 reaction. This adds further support in the favour of the above reaction.

(b) By an excited alkene molecule

According to the earlier studies of Cvetanovic(5, 35) the excited alkene molecule formed splits into a β methyl allyl radical and a hydrogen atom.



$$\left(\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>C = CH_2\right)^* \longrightarrow CH_3-\overset{}{\underset{\displaystyle CH_2}{C}}= CH_2 + H$$

The methyl allyl radical can add oxygen to give the methyl allyl peroxy radical which can decompose giving the methacrylaldehyde and a hydroxyl radical or can form the hydroperoxide on reaction with a further RH molecule as described previously.

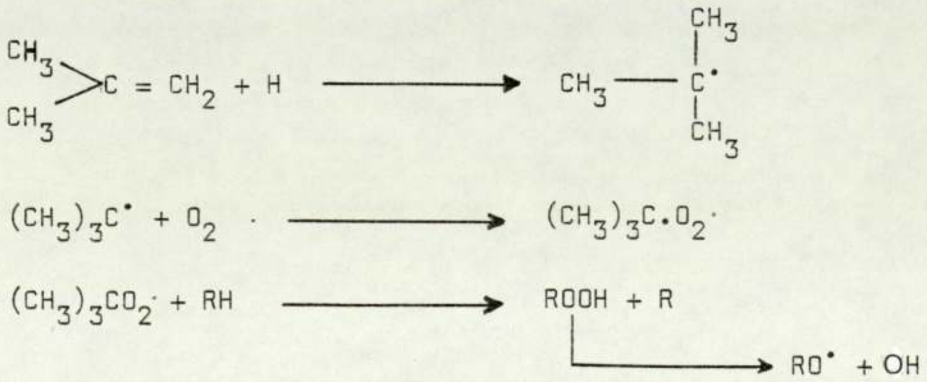
Of the above mentioned two reactions, the reaction (a) is thought to be the major source of methacrylaldehyde in the light of the experimental results. The slight increase in the yields at high alkene/O_2 ratio in both high and low pressure studies may be due to the higher rate of the reaction

$$O_2^* + \;>C = C< \longrightarrow \text{Products}$$

nevertheless a small contribution from reaction (b) in the presence of a large excess of alkene cannot be neglected.

Tertiary butanol

The most likely source of t-butanol is through t-butyl radicals formed by the addition of H-atoms to the alkene. Cvetanovic(55) has stated that any free hydrogen atoms would readily add to the excess isobutene to form tertiary butyl radicals. These and their further reactions can account for the observed t-butanol in the products.



$$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>C = CH_2 + H \longrightarrow CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C^\bullet}}$$

$$(CH_3)_3C^\bullet + O_2 \longrightarrow (CH_3)_3C.O_2^\cdot$$

$$(CH_3)_3CO_2^\cdot + RH \longrightarrow ROOH + R$$

$$ROOH \longrightarrow RO^\bullet + OH$$

The tertiary butoxy radical which is the immediate precursor of the alcohol can abstract the hydrogen from the parent hydrocarbon as follows:

$$RO^{\bullet} + RH \longrightarrow ROH + R.$$

$$(CH_3)_3.CO + RH \longrightarrow (CH_3)_3C.OH + R^{\bullet} \qquad (a)$$

In hydrocarbon-oxygen mixtures tertiary butoxy radicals can also originate through the reaction

$$RO_2 + RO_2 \longrightarrow 2RO^{\bullet} + O_2$$

In addition to the above reaction (a), a similar type of the process merits some consideration for the formation of tertiary butanol.

$$RO^{\bullet} + HO_2 \longrightarrow ROH + O_2$$

$$(CH_3)_3CO + HO_2 \longrightarrow (CH_3)_3COH + O_2 \qquad (b)$$

The likely source of hydrogen atoms is through the decomposition of the excited alkene molecule and during the formation of 2-methyl propanal as described before. The yield of tertiary butanol increase as the ratio alkene/O_2 is increased and the yield decreases in the presence of a large concentration of molecular oxygen. This shows the relative importance of reaction (a) over (b). Also it has been claimed that the presence of a large excess of molecular oxygen seems to prevent the formation of t-butanol from the tertiary butoxy radicals.[218] The same is true for the present system.

It can be seen that a combination of the schemes described accounts generally for the main observed products and the pressure change and other phenomena during the course of analysis.

6.4 MINOR PRODUCTS

The minor products obtained from the oxidation of 2-methyl propene were propanal, acetaldehyde and 2-butanone identified by the techniques described in Chapter Three. Their very low yields especially in the case of acetaldehyde and 2-butanone suggested that they may have been formed in the system due to the impurities present in the alkene under study.

Propanal and 2-butanone can be attributed to butene-1 present as an impurity and acetaldehyde could have resulted due to the reaction of ozone with propene present as an impurity in the alkene under study (2-methyl propene).

Further support for the above view comes from the fact that both propanal and acetaldehyde were detected as one of the main products during the oxidation studies of propene and butene-1 as will be described in the forthcoming chapter.

6.5 THERMOCHEMISTRY

Up until now, the possibility of various reactions already described have been assessed purely on their ability to explain the product formation and the influence of various factors such as pressure, different alkene/O_2 ratio, etc., on the yields. It is important at this stage to consider their feasibility on thermochemical grounds.

The estimated heats of the more important reactions of 2-methyl propene, propene and butene-1 are provided in Table 6.5. The heats of formation ΔH_{f_0} of products, reactants and related compounds were taken from the literature and the references to the sources of data and methods of estimation are given below.

(a) Standard data from

(i) Stull, D.R., Westrum, E.F., and Sinke, G.C.
'The Chemical Thermodynamics of Organic Compounds'
John Wiley and Son, 1st Edition (1969).

(ii) Benson, S.W.

'Additivity Rules for Estimation of Thermochemical Properties'.

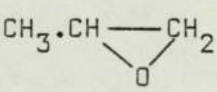
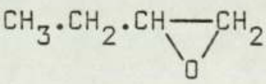
Chem. Revs. 69, 279, (1969).

(b) Estimation of ΔHfo (ROOH) was taken from

ΔHf^{o} (ROOH) - ΔHf^{o}(1-hexylOOH) = ΔHf^{o}(2 methyl propene) - ΔHf^{o}(n-hexane).

TABLE 6.5.

Heats of Reaction of some important Processes

No.	Reaction	ΔH kJ mol^{-1}	Method
1.	$O_2^* + (CH_3)_2C = CH_2 \longrightarrow CH_2 = C(CH_3)CH_2OOH$	-172	a, b
2.	$O_3 + (CH_3)_2C = CH_2 \longrightarrow (CH_3)_2.CH.CHO + O_2^*$	-234	a
3.	$O_3 + (CH_3)_2C = CH_2 \longrightarrow (CH_3)_2CO + CH_2O + \frac{1}{2}O_2$	-450.5	a
4.	$O_2^* + CH_3.CH = CH_2 \longrightarrow CH_2 = CH.CHO + H_2O$	-457.0	a
5.	$O_3 + CH_3.CH = CH_2 \longrightarrow CH_3.CHO + H.CHO + \frac{1}{2}O_2$	-444.0	a
6.	$O_3 + CH_3.CH = CH_2 \longrightarrow CH_3.CH_2.CHO + O_2^*$	-259	a
7.	$O_3 + CH_3.CH_2.CH = CH_2 \longrightarrow CH_3.CH_2.CH_2.CHO + O_2^*$	-252	a
8.	$O_3 + CH_3.CH_2.CH = CH_2 \longrightarrow CH_3.CH_2.CHO + CH_2O + \frac{1}{2}O_2$	-449	a
9.	$O^3P + CH_3.CH = CH_2 \longrightarrow$  $CH_3.\underset{\diagdown O \diagup}{CH-CH_2}$	-360	a
10.	$O^3P + CH_3.CH = CH_2 \longrightarrow CH_3.CH_2.CHO$	-459	a
11.	$O^3P + CH_3.CH_2.CH = CH_2 \longrightarrow$  $CH_3.CH_2.\underset{\diagdown O \diagup}{CH-CH_2}$		
12.	$O^3P + CH_3.CH_2.CH = CH_2 \longrightarrow CH_3.CH_2.CH_2.CHO$	-472	a
13.	$O^3P + CH_3.CH_2.CH = CH_2 \longrightarrow CH_3.CH_2.CO.CH_3$	-505.0	a
14.	$^{\cdot}OH + (CH_3)_2C = CH_2 \longrightarrow (CH_3)_2CHCHO + H$	- 12	a

It appears from the results shown in Table 6.5 that all the important reactions are favourable on thermochemical grounds. (All of them are exothermic.) It is hence anticipated that the mechanisms derived satisfactorily describes the mercury photo-sensitized oxidation of 2-methyl propene with molecular oxygen. A summary of the main points of the reaction is given below.

6.6 SUMMARY OF THE REACTION

The main product of the reaction methacrylaldehyde is thought to be formed mostly by the singlet oxygen mechanism. The more important reactions for the formation of the major products are suggested as follows:

Acetone

$$(CH_3)_2C = CH_2 + O_3 \longrightarrow (CH_3)_2CO + CH_2O$$

2-Methyl propanal

$$(CH_3)_2C = CH_2 + {}^{\bullet}OH \longrightarrow (CH_3)_2CH.CHO + {}^{\bullet}H$$

Methacrylaldehyde

$$(CH_3)_2C = CH_2 + {}^1O_2{}^* \longrightarrow CH_2 = C(CH_3).CHO + H_2O$$

Tert. Butanol

$$(CH_3)_3CO\cdot + RH \longrightarrow (CH_3)_3COH + R^{\bullet}$$

In the high pressure region > about 300 m.m. the yields of the major products are low, suggesting the importance of collisional stabilization of the intermediates formed in the system.

When the alkene/O_2 ratio is increased, the yield of those products derived from the excited oxygen molecule will decrease owing to the early consumption of excited oxygen molecule through the reaction

$$O_2^* + RH \longrightarrow \text{Products}$$

and also due to the relative unimportance of the reaction

$$O_2^* + O_2 \longrightarrow O_3 + O$$

The increase in the yields of tert. butanol have been attributed to the increasing importance of the reaction

$$RO\cdot + RH \longrightarrow ROH + R.$$

The slight increase in the yields of methacrylaldehyde when the amount of alkene is increased in the system suggested an excited alkene formation to be important to some extent for its formation. The increased yields at low pressures especially at high alkene/O_2 ratio should be expected due to the higher rate of decomposition of the intermediate responsible for the formation of methacrylaldehyde. The results show this tendency to be true.

CHAPTER SEVEN

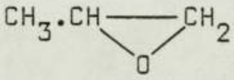
DISCUSSION OF THE MERCURY PHOTOSENSITIZED OXIDATION WITH PROPENE AND BUTENE-1

7.1 REACTION WITH PROPENE

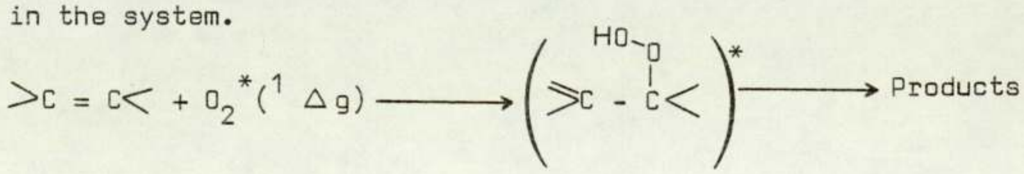
The major products obtained through the oxidation with propene were acrylaldehyde, acetaldehyde, 1-2 epoxy propane and propanal. Minor products obtained were methacrylaldehyde and 2-butanone.

Below are listed the principal observed products and their relative yields at both high and low pressures at room temperature.

TABLE 7.1

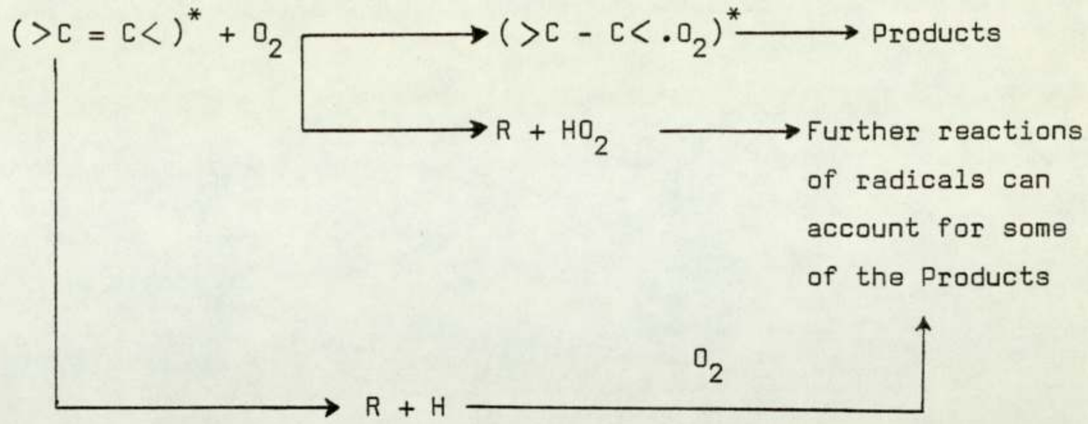
PRODUCTS	P_{Total} 600 m.m.Hg	P_{Total} 100 m.m.Hg
	Yields at alkene/O_2 1 : 10	Yields at alkene/O_2 1 : 10
$CH_3.CHO$	4.0	31
 $CH_3.CH-CH_2$ (O)	16.0	18
$CH_3.CH_2.CHO$	9.0	8
$CH_2 = CH.CHO$	32.0	90

It has been discussed in the previous chapter that the following reactions are important and may be responsible for the observed products in the system.

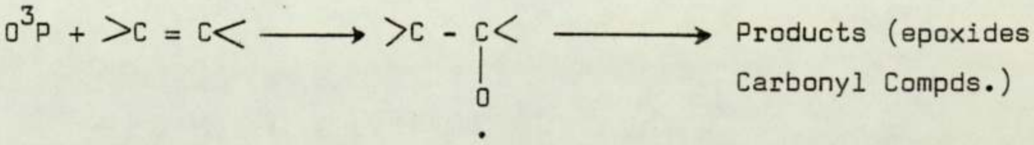
(a) 

$$>C = C< + O_2^{*}(^1 \Delta g) \longrightarrow \left(>C - \overset{HO-O}{\overset{|}{C}}< \right)^{*} \longrightarrow \text{Products}$$

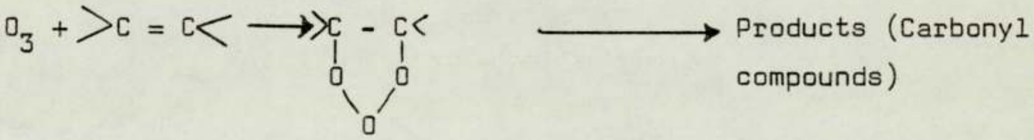
(b)



(c)



(d)



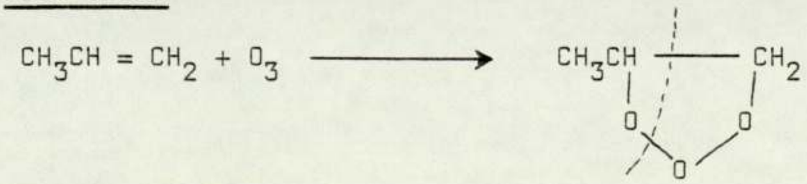
An attempt will now be made to try to find the plausible origins of each of the products and to satisfactorily explain their dependencies on various parameters.

7.1(a). MAJOR PRODUCTS AND THE POSSIBLE ROUTES FOR THEIR FORMATION.

Acetaldehyde

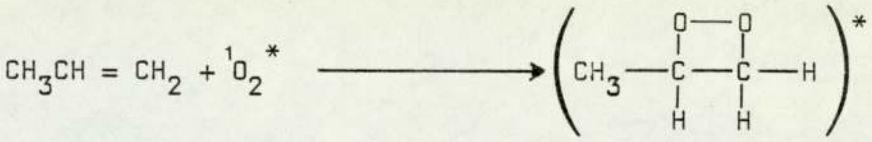
The formation of acetaldehyde can be discussed through the following reactions.

(a) From ozone



fragmentation $\longrightarrow CH_3.CHO + CH_2O$.

(b) From $O_2^{*\,1}\Delta g$



dioxetane intermediate

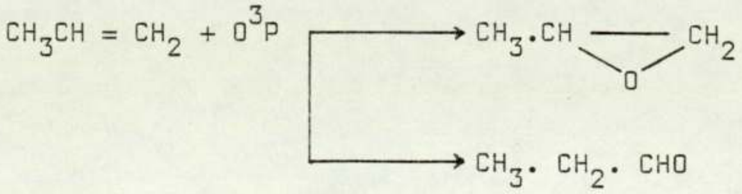
$$\longrightarrow CH_3.CHO + CH_2O$$

Reaction (b) can be discounted on the grounds that the dioxetane intermediates are less probable in the singlet oxygen reactions as explained before. Acetaldehyde can also be formed through O^3P atoms(15) but it is a minor product and cannot explain the large yields in the present case. In view of the fact that acetaldehyde is the major product of the vapour phase ozone reaction with propene and also in the previous study ozone was thought to be responsible for a major product acetone under the same mechanism, hence it is assumed that the reaction (a) is the most likely source for the acetaldehyde formation. The low yields at high pressures also supports the above view.

1-2 epoxypropane and propanal

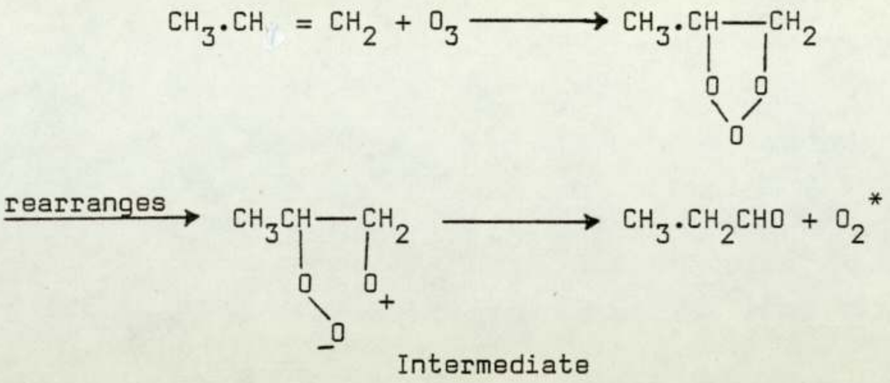
The presence of 1-2 epoxy propane and propanal among the products points towards the presence of oxygen atoms in the system. The following reactions can be thought as important for their formation.

(a) From O^3P



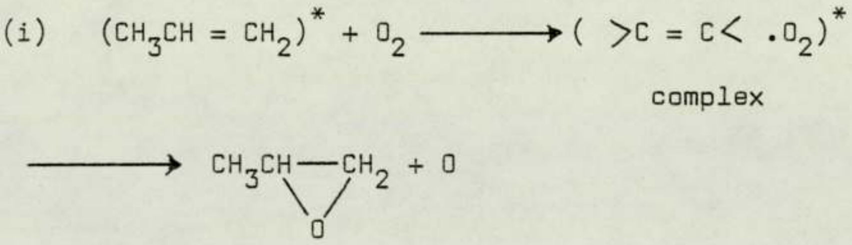
The above reaction has been described well before.

(b) From O_3

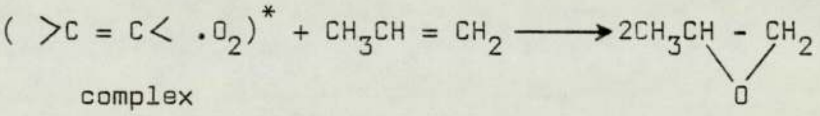


(c) From excited alkene molecule

(i)



(ii) the complex may react with another alkene molecule to give the epoxide(205).



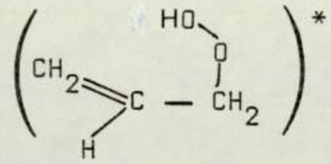
Of all the reactions discussed above, the most likely source of both 1-2 epoxy propane and propanal is through reaction (a), i.e. through O^3P atoms. The similar trends observed during the pressure dependant studies also supports this view. A small contribution from reaction (b) can be accepted on the grounds that the reaction of ozone with propene gives a small amount of propanal attributed to the splitting of some molecular oxygen from the intermediate which then rearranges to form the aldehyde. The reaction (c) cannot be responsible for the observed epoxide in the sense that although the studies under different alkene/O_2 ratio could not be performed due to the non-availability of propene gas at that time, but two or three runs done with a large excess of alkene did not show any increased yields in the epoxide formation. Hence in the light of the above views, it can be assumed that O^3P atoms are the main source of both the products.

Acrylaldehyde

The possible sources of acrylaldehyde are given below.

(a) From $O_2^*(^1\Delta g)$

$$CH_3CH = CH_2 + {}^1O_2 \longrightarrow$$



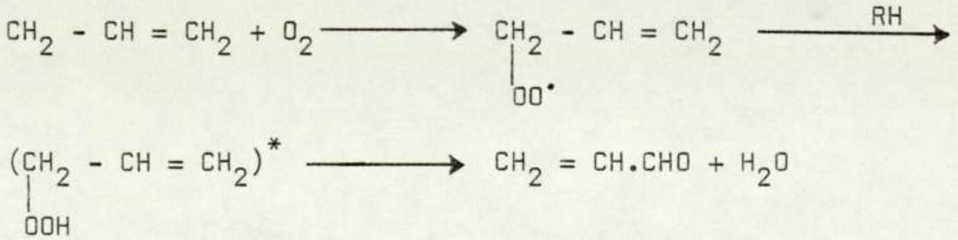
$$\longrightarrow CH_2 = CH.CHO + H_2O$$

The above mechanism is same as that derived for the formation of methacrylaldehyde in the previous chapter and needs no further explanation. The above reaction is also favoured by the microwave experiments (see the results quoted in Chapter Five).

(b) From an excited alkene molecule

$$(CH_3CH = CH_2)^* \longrightarrow CH_2 - CH = CH_2 + H$$

Dissociation of the excited propene molecule into an allyl radical and a hydrogen atom is known from the earlier studies.(5, 35) The allyl radical can add oxygen to give allyl peroxy radical which on reaction with a further alkene molecule can give the hydroperoxide which is supposed to be the source of acrylaldehyde.



$$CH_2 - CH = CH_2 + O_2 \longrightarrow \underset{OO^\cdot}{CH_2} - CH = CH_2 \xrightarrow{RH}$$

$$(\underset{OOH}{CH_2} - CH = CH_2)^* \longrightarrow CH_2 = CH.CHO + H_2O$$

allyl hydroperoxide

Considering the above two processes, it seems that process (a) is mainly responsible for the observed acrylaldehyde in the system. During some runs with a high percentage of alkene in the system it was noted that there was a slight increase in the yield of acrylaldehyde which indicates a slight contribution from reaction (b) as well. The conclusions reached for the formation of methacrylaldehyde in the study of 2-methyl propene also supports the above view.

7.1(b) MINOR PRODUCTS

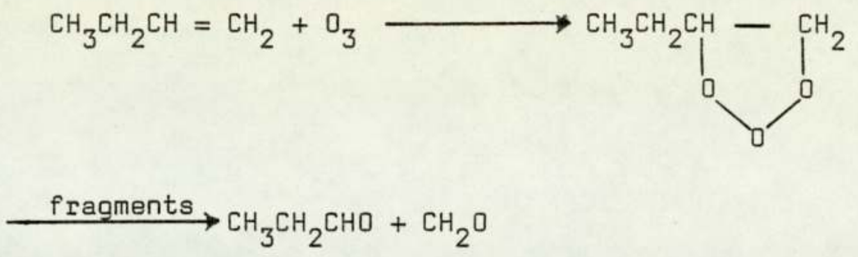
The minor products identified were methacrylaldehyde and 2-butanone. The yields of both the compounds were low. The presence of methacrylaldehyde and 2-butanone among the products suggests the presence of compounds with four carbon atoms. This points towards the presence of butenes as impurities in the alkene under study, mainly 2-methyl propene as it can account for both of the products.

7.2 REACTION WITH BUTENE-1

The studies of the mercury photosensitized oxidation of butene-1 could not be completed due to the shortage of time. Nevertheless, the few results of the reaction were quite useful in providing more insight towards the mechanism of the product formation.

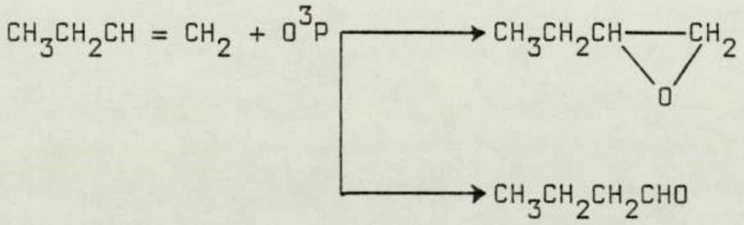
The main products detected were propanal, α -butene oxide and n-butanal. A minor product 2-butanone was also detected. Rest of the products were not identified and the studies for the above reaction had to be abandoned at this stage.

In the light of the previous reactions (with propene and 2-methyl propene) it can be assumed that the propanal may have arrived by the ozone mechanism.

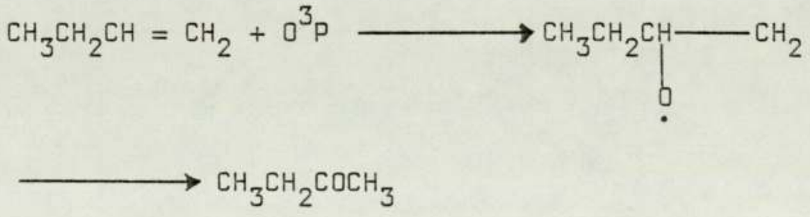


The above reaction is feasible on thermochemical grounds having a high exothermicity.

Similarly the formation of α -butene oxide and n-butanal could be explained through the simple oxygen atom O^3P mechanism.



The minor product 2-butanone may have been formed by the substitution of O^3P atoms to the more substituted carbon atom of the alkene following the migration of a hydrogen atom to the other carbon atom.



$$CH_3CH_2CH = CH_2 + O^3P \longrightarrow CH_3CH_2\underset{\underset{\cdot}{O}}{CH}-CH_2 \longrightarrow CH_3CH_2COCH_3$$

The present work agrees in some respects with some of the previous observations. In comparing and assessing the results of such studies, it should be noted that the system under study was quite complex where O_2^*, O_3, O and other reactive species were present and each contributing at least to some extent towards the presence of the observed products. Appreciable quantities of relatively hot unstable compounds (of peroxidic nature) may have been formed initially and hence the amounts and the types of the final stable products observed will depend on the conditions under which the fragmentation and degradation took place.

7.3 CONCLUSIONS

The mercury photosensitized oxidation of hydrocarbons in the gas phase namely with some alkenes has been performed. It has been noted that molecular oxygen with its species O_2^* (in $^1\Delta g$ state), O_3, O and the other reactive species are each responsible up to some extent for the formation of the products observed in the system.

A reasonably satisfactory explanation has been made for the formation of the products which has been shown to be reasonably consistent with the observed variations in product yields with the reaction parameters.

An important feature of the reaction was some of the similarities observed (especially in the case of 2-methyl propene) between the singlet oxygen (from microwave discharge)/alkene reaction and the Hg^*/O_2/alkene reaction. This indicated some participation of the $^1O_2^*$ (preferably in $^1\Delta g$ state) in the system under study.

Another notable feature of the reactions is the presence of those carbonyl products in significant amounts which are the predominant products in the vapour phase reaction of ozone with these alkenes, for example acetone in the case of 2-methyl propene, acetaldehyde in the case of propene and propanal in the case of butene-1. This suggests the presence of significant amounts of ozone in the system, and it is quite likely that there may be some other intermediate formation of ozone apart from the two main ozone producing reactions.

$$\left.\begin{array}{l} O_2 + O_2 \longrightarrow O_3 + O \\ \text{and} \\ O + O_2 + M \longrightarrow O_3 + M \end{array}\right\} \quad \phi = 0.14 \; (184)$$

It is noted that at high pressures the yield of the major products decrease which apart from the explanations already made elsewhere can be attributed to the low rate for thermally decomposition and unstability of the reaction intermediates.

In the reaction of 2-methyl propene the little increase in the amounts of methacrylaldehyde at high alkene/O_2 ratio indicated some participation of the excited alkene molecule as well for its formation. Similar trend was observed for acrylaldehyde as well.

The minor product formation was not of much significance in the system and it may have been due to the impurities present in the starting material.

A fact which remained unsolved was the absence of isobutene oxide among the products from 2-methyl propene and hence the non-participation of oxygen atoms was to be assumed in that case. In the propene and butene-1 reactions the corresponding epoxides were detected and identified and the results strongly indicated the participation of oxygen atoms in both the above cases. It is difficult to say at the moment why the two systems should differ under the conditions used. Perhaps further work in this connection would provide the answer.

The microwave experiments with the above alkenes provided valuable information and insight towards the origin of some of the major products which were otherwise difficult to prove by alternative techniques. Results were quite helpful. A detailed product analysis would have been fruitful in providing more information about the nature of singlet oxygen reactions in the gas phase but unfortunately the time factor prevented this.

In the end it would be necessary to state that all the reaction schemes have been interpreted purely on the product identification and the influence of various parameters and with large errors being possible in measuring the quantum yields of the products and in view of the uncertainties mentioned before and the lack of information on the exact nature of the intermediate peroxidic substances the present results provide a limited picture of these complex gas phase reactions. However, a preliminary broad survey has been made for some of the alkenes, and it is hoped that the information obtained may supplement the observations of other workers in this field.

Further research in this field, especially by varying the alkene/O_2 ratio over a wide range, by studying the temperature dependence of the reactions and a detailed product analysis from ${}^1O_2{}^*$ and O_3 reactions with alkenes in the present system would provide much insight towards the mechanism and may prove an interesting problem for further research, especially by estimating the rate constants and other Arrhenius parameters for the three systems (${}^1O_2{}^*$/alkene, Hg^*/O_2/alkene, O_3/alkene) and comparing them.

REFERENCES

1. FRANCK, J. Z. Physik. 9, 259, (1922).

2. CARIO, G., and FRANCK, J. Z. Physik. 11, 161, (1922).

3. ENGEL, P.S., and MONROE, B.M. Adv. in Photochemistry, Vol. 8. 245, (1971).

4. STEACIE, E.W.R. Can.J.Res. B26, 609, (1948).

5. CVETANOVIC, R.J. Progress in Reaction Kinetics. 2, 39 - 130, (1964).

6. GUNNING, H.E., and STRAUSS, O.P. Adv. in Photochemistry, Vol. 1, 209 - 274, (1963).

7.(a)LAIDLER, K.J. J. Chem. Physics. 10, 43, (1942).
 (b) ibid 10, 34, (1942).
 (c) ibid 15, 712, (1947).

8. PRINGSHEIM, P. Fluoroscence & Phosphorescence, Inter Science Publishers, New York. (1949).

9. MITCHELL, A.C.G., and ZEMANSKY, M.W. Resonance Radiation and Excited Atoms. Cambridge University Press (1934), Reprinted (1961).

10. BOWEN, E.J. Chemical Aspects of Light, 2nd Edition, Oxford University Press, Oxford, (1946).

11. NOYES, W.A., and LEIGHTON, P.A. The Photochemistry of Gases, Reinhold Publishing Corp., New York. (1941).

12. ROLLEFSON, G.K., and BURTON, M. Photochemistry, Prentice Hall, Eaglewood Cliffs, N.J. (1939).

13. PITTS, J.N., WILKINSON, F., and HAMMOND, G.S. Adv. in Photo-Chemistry, Vol. 1., 16, (1963).

14. CALLEAR, A.B., and NORRISH, R.G.W. Proc. Roy. Soc., London. A266, 299, (1962).

15. CVETANOVIC, R.J. Adv. in Photochemistry, Vol.1, 115, (1963).

16. CALLEAR, A.B., and HEDGES, R.E.M. Trans. Faraday Soc., 66, 605, (1970).

17. KANG YANG. J. Amer. Chem. Soc., 89, 5344, (1967).

18. MICHAEL, J.V., and YEH, C. J. Chem. Phys., 53, 59, (1970).

19. CALLEAR, A.B., and HEDGES, R.E.M. Trans. Faraday Soc., 66, 615, (1970).

20. HORNE, D.G., GOSAVI, R., and STRAUSZ, O.P. J. Chem. Phys., 48, 4758, (1968).

21. MARCUS, R.A., DARWENT, B., and STEACIE, E.W.R. J. Chem. Phys., 16, 987, (1948).

22. POTTIE, R.F., HARRISON, A.G., and LOSSING, F.B. Can. J. Chem., 39, 102, (1961).

23. TAKAZAKI, Y., MORI, S., and KAIVASAKI, H. Chem. Soc. Japan, 39, 1643, (1966).

24. MASON, C.R., and STEACIE, E.W.R. J. Chem. Phys., 18, 210, (1950).

25. JENNINGS, K.R., and CVETANOVIC, R.J. J. Chem. Phys., 35, 1233, (1961).

26. BACK, R.A. Trans. Faraday Soc., 54, 512, (1958).

27. BACK, R.A. Can. J. Chem., 37, 1834, (1959).

28. CVETANOVIC, R.J., FALCONER, W.E., and JENNINGS, K.R. J. Chem. Phys., 35, 1225, (1961).

29. CVETANOVIC, R.J. Paper presented to the Royal Society of Canada, Annual Meeting, Edmonton (1958), Proc. & Trans. Roy. Soc. Can., 52, (Abstract).

30. LEROY, D.J., and STEACIE, E.W.R. J. Chem. Phys, 9, 829, (1941).

31. LEROY, D.J., and STEACIE, E.W.R. J. Chem. Phys, 10, 676, (1942).

32. CVETANOVIC, R.J., and CALLEAR, A.B. J. Chem. Phys., 23, 1182, (1955).

33. CALLEAR, A.B., and CVETANOVIC, R.J. J. Chem. Phys., 24, 873, (1956).

34. SETSER, D.W., RABINOWITCH, B.S., and PLACZEK, D.W. J. Am. Chem. Soc., 85, 862, (1963).

35. LOSSING, F.P., MARSDEN, D.G.H., and FARMER, J.B. Can. J. Chem., 34, 701, (1956).

36. AVRAHAMI, M., and KEBARLE, P. J. Phys. Chem., 67, 354, (1963).

37. CVETANOVIC, R.J., and DOYLE, L.C. J. Chem. Phys., 37, 543, (1962).

38. MAJER, J.R., MILE, B., and ROBB, J.C. Trans. Faraday Soc., 57, 1342, 1692, (1961).

39. CUNDALL, R.B., and PALMER, T.F. Trans. Faraday Soc., 57, 1211, (1960).

40. KEBARLE, P., and AVRAHAMI, M. J. Chem. Phys., 38, 700, (1963).

41. ARAI, S., and SHIDA, S. J. Chem. Phys., 38, 694, (1963).

42. MANNING, W.M., and NOYES, W.A. J. Amer. Chem. Soc., 54, 3907, (1932).

43. CVETANOVIC, R.J. J. Chem. Phys., 23, 1203, (1955).

44. CVETANOVIC, R.J. J. Chem. Phys., 23, 1208, (1955).

45. MROZOWSKI, S. Z. f. Phys., 78, 826, (1932).

46. ZUBER, K. Helv. Phys. Acta, 8, 487, (1935).
ibid 9, 285, (1936).
ibid Nature, 136, 796, (1935).

47. McDONALD, C.C., and GUNNING, H.E. J. Chem. Phys., 20, 1817, (1952).

48. BILLINGS, B.H., HITCHCOCK, W.J., and ZELIKOFF, M. J. Chem. Phys., 21, 1762, (1953).

49. ZELIKOFF, M., ASCHENBRAND, L.M., and WYCKOFF, P.H. J. Chem. Phys., 21, 376, (1953).

50. GUNNING, H.E. Can. J. Chem., 36, 89, (1958).

51. DESNOYER, M., NIEF, G., and ROTH, E. 12th Annual Meeting of the Physical Chemistry Society, Paris, June 4-8, (1962). Physical Chemistry of isotope separation.

52. DINGLE, T., and GUNNING, H.E. Unpublished data.

53. CVETANOVIC, R.J. J. Chem. Phys., 23, 1375, (1955).

54. CVETANOVIC, R.J. J. Chem. Phys., 25, 376, (1956).

55. CVETANOVIC, R.J. Can. J. Chem., 36, 623, (1958).

56. CVETANOVIC, R.J., and DOYLE, L.C. Can. J. Chem., 38, 2187, (1960).

57. HEICKLEN, J., and COHEN, N. Adv. in Photochemsitry, Vol. 5, 157, (1967).

58. SAUNDERS, D., and HEICKLEN, J. J. Phys. Chem., 70, 1950, (1966).

59. COHEN, N., and HEICKLEN, J. J. Phys. Chem, 70, 3082, (1966).

60. HEICKLEN, J., COHEN, N., and SAUNDERS, D. J. Phys. Chem., 69, 1774, (1965).

61. HEICKLEN, J., and KNIGHT, V. J. Phys. Chem., 70, 3893, (1966).

62. HEICKLEN, J., and KNIGHT, V. J. Chem. Phys., 47, 4203, (1967).

63. SAUNDERS, D., and HEICKLEN, J. J. Amer. Chem. Soc., 87, 4062, (1965).

64. MITCHELL, K.C., and SIMONS, J.P. J. Chem. Soc. (B), 1005, (1968)

65. MOSS, S.J., and JENNINGS, K.R. Trans. Faraday Soc., 64, 686, (1968).

66. MORLEY, J.G. Ph.D. Thesis, University of Sheffield, (1970).

67. JONES, D.S. Ph.D. Thesis, University of Aston in Birmingham, (1972).

68. RATTANAPHANI, S. Ph.D. Thesis, University of Aston in Birmingham, (1973).

69. MOSS, S.J., and JENNINGS, K.R. Trans. Faraday Soc., 65, 415, (1969).

70. MOSS, S.J. Trans. Faraday Soc., 67, 3503, (1971).

71. SCHENCK, G.O., and GOLLNICK, K. References cited in Pure & Appl. Chem., Vol. 9, 507, (1964).

72. LIVINGSTON, R. "Photochemical Autoxidation" in Auto-oxidation and Antioxidants, Vol. 1, W.O. Lundberg Ed: Interscience, New York, p.249, (1961).

73. HOCHSTRASSER, R.M., and PORTER, G.B. "Primary processes in Photo-oxidation" in Quart. Rev., 14, 146, (1960).

74. GOLLNICK, K., and SCHENCK, G.O. "Oxygen as Dienophile". Adv. in Photochemistry, Vol. 6, 115, (1968).

75. GOLLNICK, K. Adv. in Photochemistry, Vol. 6, p.1 - 122, (1968).

76. FOOTE, C.S., and WEXLER, J. Am. Chem. Soc., 86, 3879, 3880, (1964).

77. GAFFRON, H. Chem. Ber., 60, 755, (1927).

78. GAFFRON, H. Biochem. Z., 264, 251, (1933).

79. GAFFRON, H. Z. Physik. Chem., B37, 437, (1937).

80. BOWEN, E.J., and STEADMAN, F. J. Chem. Soc. (Lond.), 1098, (1934).

81. KOBLITZ, W., and SCHUMACHER, H.J. Z. Physik. Chem., B 35, 11, (1937).

82. SCHUMACHER, H.J. Z. Physik. Chem., B 37, 462, (1937).

83. SCHONBERG, A. Ann. Chem., 578, 299, (1935).

84. KAUTSKY, H., and HIRSCH, A. Chem. Ber., 64, 2677, (1931).

85. KAUTSKY, H., and DE BRUIJIN, H. Naturwiss, 19, 1043, (1931).

86. KAUTSKY, H., DE BRUIJIN, H., NEUWIRTH, R., and BAUMEISTER, W. Chem. Ber., 66, 1588, (1933).

87. KAUTSKY, H., HIRSCH, A., and FLESCH, W. Chem. Ber., 68, 152, (1935).

88. KAUTSKY, H. Biochem. Z., 291, 271, (1937).

89. ELLIS, I.W., and KNESER, H.O. Z. Physik., 86, 583, (1933).

90. SCHENCK, G.O. Naturwiss, 35, 28, (1948).

91. SCHENCK, G.O., and KINKEL, K. Naturwiss, 38, 355, (1951).

92. SCHENCK, G.O. Habilitations - Schrift, University of Halle, (1943).

93. SCHENCK, G.O. Naturwiss, 40, 205, 229, (1953).

94. SCHENCK, G.O. Angewchem., 69, 579, (1957).

95. ROSENBERG, J.L., and SHOMBERT, D.J. J. Amer. Chem. Soc., 82, 3527, (1960).

96. COREY, E.J., and TAYLOR, W.C. J. Amer. Chem. Soc., 86, 3881, (1964).

97. ARNOLD, S.J., OGRYZLO, E.A., and BROWNE, R.J. Photochem. Photobiol., 4, 903, (1965).

98. TROZZOLO, A.M., and FAHRENHOLTZ, S.R. Annals, N.Y. Acad. of Sci., Vol. 171, 61, (1970).

99. FOOTE, C.S. Acct. Chem. Res., 1, 104, (1968).

100. SCHENCK, G.O. Annals, N.Y. Acad. of Sci., Vol. 171, 67, (1970).

101. GOLLNICK, K., FRANKEN, T., SCHADE, G., and DORHOFER, G. Annals, N.Y. Acad. of Sci., Vol. 171, 89, (1970).

102. ARNOLD, S.J., KUBO, M., and OGRYZLO, E.A. Advan. Chem. Ser., 77, 133, (1968).

103. KASHA, M., and KHAN, A.U. Annals, N.Y. Acad. of Sci., Vol. 171, 5, (1970).

104. KAWAOKA, K., KHAH, A.U., and KEARNS, D.R. J. Chem. Phy., 47, 1883, (1967).

105. HERZBERG, G. Molecular Spectra and Molecular Structure Spectra of diatomic Molecules, 2nd Edn., D. Van Nosterand Co., New York, N.Y., p.560, (1950).

106. KHAN, A.U., and KASHA, M. J. Amer. Chem. Soc., 88, 1574, (1966).

107. McKEOWN, E., and WATERS, W.A. Nature, 203, 1063, (19).

108. McKEOWN, E., and WATERS, W.A. J. Chem. Soc., B, 1040, (1966).

109. WASSERMAN, H.H., and SCHEFFER, J.R. J. Amer. Chem. Soc., 89, 3073, (1967).

110. KHAN, A.U., and KASHA, M. J. Chem. Phys., 39, 2105, (1963).

111. KHAN, A.U., and KASHA, M. Nature, 204, 241, (1964).

112. FOOTE, C.S., WEXLER, S., ANDO, W., and HIGGINS, R. J. Amer. Chem. Soc., 90, 975, (1968).

113. KHAN, A.U. Submitted for Publications.

114. KHAN, A.U., and KEARNS, D.R. Adv. Chem. Ser., 77, 143, (1968).

115. ARNOLD, S.J., OGRYZLO, E.A., and WITZKE, H. J. Chem. Phys., 40, 1769,

116. KAPLAN, J. Nature, 159, 673, (1947).

117. KAPLAN, J. Phys. Rev., 71, 274, (1947).

118. FONER, S.N., and HUDSON, R.L. J. Chem. Phys., 25, 601, (1956).

119. KEARNS, D.R., KAWAOKA, K., and KHAN, A.U. J. Chem. Phys., 46, 1842, (1967).

120. (a) KEARNS, D.R., and CHAMBERS, R.W. Unpublished results.
(b) KEARNS, D.R., RADLICK, P., and HOLLINS, R.A. Unpublished results.

121. PITTS, J.N. Annals, N.Y. Acad. of Sci., Vol. 171, 239, (1970).

122. GOLLNICK, K. Adv. Chem. Ser., 77, 78, (1968).

123. ALDER, K., and SOLL, H. Ann. Chem., 565, 73, (1949).

124. SCHONBERG, A. Preparative Organische Photochemie Springer-verlag, Berlin, V, (1958).

125. SCHENCK, G.O., GOLLNICK, K., BUCHWALD, G., SCHROETER, S., and OHLOFF, G. Ann. Chem., 674, 93, (1964).

126. SCHENCK, G.O., NEUMULLER, O.A., OHLOFF, G., and SCHROETER, S. Ann. Chem., 687, 26, (1965).

127. SCHENCK, G.O. Angew. Chem., 64, 12, (1952).

128. SCHENCK, G.O., and SCHULTE-ELTE, K.H. Unpublished.
K.H. SCHULTE-ELTE, dissertation, University of Gottingen (1961).

129. NICKON, A., and BAGLI, J.F. J. Amer. Chem. Soc., 81, 6330, (1959).

130. NICKON, A., and BAGLI, J.F. J. Amer. Chem. Soc., 83, 1498, (1961).

131. McCAPRA, F. Quart. Rev., 20, 485, (1966).

132. FOOTE, C.S., and LIN, J.W.P. Tetrahedron Letters, 3267, (1968).

133. FENICAL, W., KEARNS, D.R., and RADLICK, P. J. Amer. Chem. Soc., 91, 3396, (1969).

134. SHARP, D.B. Abstracts 138th National Meeting of the Amer. Chem. Soc., New York, (1969).

135. FENICAL, W., KEARNS, D.R., and RADLICK, P. J. Amer. Chem. Soc., 91, 7771, (1969).

136. KEARNS, D.R., FENICAL, W., and RADLICK, P. Annals, N.Y. Acad. of Sci., Vol. 171, 34, (1970).

137. FOOTE, C.S. Pure appl. chem., 27, (1971).

138. FALITT and NICKON, A. Adv. Chem. Ser., 77, 118, (1968).

139. FOOTE, C.S., FUJIMOTO, T.T., and CHANG, Y.C. Tetrahedron Lett., 45, (1972).

140. ASHFORD, R.D., and OGRYZLO, E.A. J. Amer. Chem. Soc., 97, 3604, (1975).

141. KOCH, F. Tetrahedron, 24, 6295, (1968).

142. NORTH, A.M. "The collision theory of chemical reactions in liquids". Methuen and Co. Ltd., London, 1964.

143. FOOTE, C.S., and DENNY, R.W. J. Amer. Chem. Soc., 93, 5168, (1971).

144. KOPECKY, K.R., and VAN de SANDE, J.H. Can. J. Chem., 50, 4034, (1972).

145. ASHFORD, R.D., and OGRYZLO, E.A. Can. J. Chem. in press.

146. OGRYZLO, E.A. Photophysiology, 5, 35, (1970).

147. CORMIER, J.C., and DEGLISE, X. Bull. Soc. Chim. Fr., 869, (1973).

148. WIGNER, A.M., and BAYES, K.D. J. Phys. Chem., 70, 302, (1966).

149. MURRAY, R.W., and KAPLAN, M.L. J. Amer. Chem. Soc., 90, 4161, (1968).

150. BROADBENT, A.D., GLEASON, W.S., PITTS Jnr., J.N., and WHITTLE, E. Chem. Commun., p.1315, (1968).

151. NOXON, J.F. Can. J. Phys., 39, 1110, (1961).

152. FONER, S.N., and HUDSON, R.L. J. Chem. Phys., 25, 601, (1956).

153. ELIAS, L.E., OGRYZLO, E.A., and SCHIFF, H.I. Can. J. Chem., 37, 1680, (1959).

154. HERRON, J.T., and HUIE, R.E. Annals, N.Y. Acad. of Sci., Vol. 171, 229, (1970).

155. GLEASON, W.S., BROADBENT, A.D., WHITTLE, E., and PITTS Jnr., J.N. J. Amer. Chem. Soc., 92, 2068, (1970).

156. VRBASKI, T., and CVETANOVIC. Can. J. Chem., 38, 1053, (1960).

157. KUMMLER, R.H. G.E. Report N-10875, (1967).

158. ELIAS, L.E. J. Chem. Phys., 38, 989, (1963).

159. WESTENBURG, A.A., and DEHAAS, N. Twelfth Symposium (International) on Combustion. The Combustion Institute, 289, (1969).

160. NIKI, H., DABY, E.E., and WEINSTOCK, B. Twelfth International Symposium on Combustion. The Combustion Institute, 277, (1969).

161. CERFONTAIN, H., and KUTSCHKE, K.O. J. Amer. Chem. Soc., 84, 4017, (1962).

162. CVETANOVIC, R.J. J. Chem. Phys., 30, 19, (1959).

163. SMITH, I.W.M. Trans. Faraday Soc., 64, 378, (1968).

164. CVETANOVIC, R.J. J. Chem. Phys., 33, 1063, (1960).

165. MARSHALL, A.L. J. Phys. Chem., 30, 34, (1926).

166. GRAY, J.A. J. Chem. Soc., 3150, (1952).

167. GRAY, J.A. J. Chem. Phys., 21, 1300, (1953).

168. NALBANDYAN, A.B. Doklady Akad Nauk S.S.S.R., 66, 413, (1949).

169. NALBANDYAN, A.B., and FOK, N.V. Doklady Akad Nauk S.S.S.R., 86, 589, (1952).

170. BURGESS, R.H., and ROBB, J.C. Trans. Faraday Soc., 54, 1015, (1958).

171. DICKINSON, R.G., and SHERRIL, M.S. Proc. Natl. Acad. Sci., U.S., 12, 175, (1926).

172. LEIPUNSKY, A.J., and SAGULIN, A.W. Z. Physik. Chem. B. 1, 362, (1928).

173. BATES, J R and TAYLOR, H S. J. Amer. Chem. Soc., 49, 2438, (1927).

174. BATES, J.R., and SALLEY, D.J. J. Amer. Chem. Soc., 55, 110, (1933).

175. BARAK, M., and TAYLOR, H.S. Trans. Faraday Soc., 28, 569, (1932).

176. EVANS, M.G. J. Chem. Phys., 2, 726, (1934).

177. MARSHALL, A.L. J. Phys. Chem., 30, 1078, (1926).

178. VOLMAN, D.H. J. Chem. Phys., 14, 707, (1946).

179. TAYLOR, H.S. Trans. Faraday Soc., 21, 562, (1925).

180. CLINE, J.E., and FORBES, G.S. J. Amer. Chem. Soc., 63, 2152, (1941).

181. VOLMAN, D.H. J. Amer. Chem. Soc., 76, 6034, (1954).

182. VOLMAN, D.H. Adv. in Photochemistry, Vol. 1, 52, (1963).

183. VOLMAN, D.H. J. Chem. Phys., 24, 122, (1956).

184. CALLEAR, A.B., PATRICK, C.R., and ROBB, J.C. Trans. Faraday Soc., 55, 280, (1959).

185. PERTEL, R., and GUNNING, H.E. Can. J. Chem., 37, 35, (1959).

186. VOLMAN, D.H., GILL, E.K., and LAIDLER, K.J. J. Chem. Phys., 30, 589, (1959).

187. FALLON, R.J., VANDERSLICE, J.T., and MASON, E.A. J. Phys. Chem., 64, 505, (1960).

188. MITCHELL, A.C.G. J. Franklin Inst., 206, 817, (1928).

189. GILL, E.K., and LAIDLER, K.J. Can. J. Chem., 36, 79, (1958).

190. HOMER, J.B., and LOSSING, F.P. Can. J. Chem., 44, 143, (1966).

191. KARL, G., KRUUS, P., and POLANYI, J.C. J. Chem. Phys., 46, 224, (1967).

192. KARL, G., KRUUS, P., POLANYI, J.C., and SMITH, I.W. J. Chem. Phys., 46, 244, (1967).

193. HOFFMAN, M.Z., GOLDWASSER, M., and DAMOUR, P.L. J. Chem. Phys., 47, 2195, (1967).

194. CHEN, S. Hua Hsueh Hsueh Pao, 23, 188, (1957).

195. DESNOYER, M., NIEF, G., and ROTH, E. J. Chim. Phys., 60, 209, (1963).

196. CALLEAR, A.B., and WILLIAMS, G.J. Trans. Faraday Soc., 60, 2158, (1964).

197. MORAND, J.P., and NIEF, G. J. Chim. Phys., 2058, (1968).

198. WARBURG, E. Z. Elektro. Chem., 27, 133, (1921).

199. ZENER, C. Proc. Roy. Soc. (London), 140, 660, (1933).

200. VANDERSLICE, J.T., MASON, E.A., and MAISCH, W.G. J. Chem. Phys., in press.

201. LAIDLER, K.J. 'The Chemical Kinetics of Excited States', Oxford University Press, London, p.31, (1955).

202. BATES, J.R. J. Am. Chem. Soc., 54, 569, (1932).

203. HEICKLEN, J., and KNIGHT, V. Report TR-669 (6250 - 40) - 1 Space Corp., June, 1966.

204. HEICKLEN, J., and KNIGHT, V. J. Phys. Chem, 70, 3901, (1966).

205. HEICKLEN, J., and JOHNSTON, T. J. Phys. Chem., 71, 1391, (1967).

206. BATEMAN, L., and GEE, G . Proc. Roy. Soc., A 195, 376, (1949).

207. WATSON, J.S., and DARWENT, B. de B. J. Phys. Chem., 61, 577, (1957).

208. BELL, K.M., and McDOWELL, C.A. Can. J. Chem., 39, 1419 - 1433, (1961).

209. TURNER, A.H., CALLEAR, A.B., and CVETANOVIC, R.J. Cited in Ref. 161.

210. EGERTON, A.C., EVRETT, A.J., MINKOFF, G.J., RUDRAKANDAN, S., and SALOOJA, K.C. Anal. Chim. Acta., 10, 422, (1954).

211. YOUNG, C.A., VOIGT, R.R., and NIEULAND, J.A. Ind. Eng. Chem. Anal. Ed., 8, 198, (1936).

212. DIETZ, W.A. J. Gas Chrom., 10, 68, (1967).

213. VRBASKI, T., and CVETANOVIC, R.J. Can. J. Chem., 38, 1063, (1960).

214. BAILEY, P.S. Chem. Revs., 58, 940, (1958).

215. CRIEGEE, R. Abstracts of Papers, 136th Meeting Amer. Chem. Soc., Atlantic City, N.J., p.87P., (1959).

216. SATO, S., and CVETANOVIC, R.J. Can. J. Chem., 36, 970, (1958).

217. WAYNE, R.P. Annals, N. Y. Acad. of Sci., Vol. 171 199, (1970).

218. HOARE, D.E., and PEARSON, G.S. Adv. in. Photochemistry., Vol. 3 83, (1964).