THE REACTIONS OF BIRADICALS

By

R.K.S. MEHTA

Thesis presented for the Degree of Doctor of Philosophy

ABSTRACT OF THESIS

Name of Candidate : Ram K.S. Mentu
Degree : Ph.D.
Date : June, 1960
Title of Thesis : THE REACTIONS OF BIRADICALS

The reactions of methylene biradicals with ethers is the main subject of this thesis. By the thermal or photochemical decomposition of ketenes, or diacetoxy methane and acetone, biradicals of the form \( \cdot \text{CH}_2 \) and \( \cdot \text{NH} \) can be produced. The stability, reactivity, and selectivity of these as some of the highly substituted carbones and imines has been reviewed in the first part.

1. The gas phase reactions of methylene generated photochemically from ketene has been found to show discrimination in attack, that C-H is attacked faster than secondary, is faster than primary as seen from the total bond reactivity figures 8.16, 4.17, 1.00 and follows the trend expected from the bond dissociation energies. The experimental insertions into 2 C-H is not far from the observed value for 3 C-H (1.00, 1.02) compared to preference shown for 2 C-H (2.79) at 100°C. In the total bond reactivity account has been taken of the abstraction rate which is large for the C-H. Besides Insertions, three novel reaction processes have been discovered in the present research.

2. Displacement Reaction where \( \text{CH}_2 \) displaces an olefin from an ether giving rise to methyl alkyl ether e.g.

\[
\text{CH}_2 + \text{C}_2\text{H}_5\text{O} + \text{H}_7 \rightarrow \text{CH}_3\text{C} + \text{C}_2\text{H}_4
\]

or

\[
\text{C}_2\text{H}_5\text{O} + \text{H}_7 \rightarrow \text{CH}_3\text{C} + \text{C}_2\text{H}_4
\]

At 100°C, attack on Et-O of EtOCH and EtOPh was about same, the value for Fr-I-O was half indicating steric effect. This reaction has been distinguished from the typical radical reactions of methylene. Possibly CHI behaves as a Lewis acid and the split of C-O bond involves a cyclic transition state. The formation of a coordinate bond of oxygen followed by an H-abstraction reaction from the adjacent carbon atom has been postulated to explain this mechanism.

3. Abstraction Reaction where CHI behaves like a monoradical and abstracts sec or tert hydrogen than producing an ether monoradical that breaks up, e.g. EtOCH was found to give acetaldehyde, EtOPh gave acetaldehyde as well as propionaldehyde. Depending upon which hydrogen (secy) is abstracted in Fr-II group, a shift of H atom from \( \alpha \) to \( \beta \) (in case of carbon) must proceed to form propionaldehyde. With Fr-I-OPh, this reaction gave acetone, along with methyl and propyl radicals. The products arising from the dimerisation, cross combination, and disproportionation of these radicals have been proved to be equimolar with acetone which lends support to the mechanism proposed herein.

4. The addition of oxygen to the system yielded peroxy radicals giving rise to large amounts of esters viz. ethyl acetate and ethyl formate from diethyl ether. Methylene abstracts hydrogen of ether and the monoradical ether combines with oxygen yields ether peroxy intermediate. Similar result was obtained using methyl radicals for H-abstraction in place of \( \text{CH}_2 \). The intermediate of the form

\[ \text{CH}_2\text{OCH}_2\text{H}_5 \] (1) could break up by any of the two steps

(a) \[ \text{CH}_2\text{O} \rightarrow \text{CH}_2\text{H}_3 + \cdot \text{OH} \]

(b) \[ \text{CH}_2\text{O} \rightarrow \text{CH}_2\text{H}_3 + \cdot \text{CH}_2\text{O} \]

where step (b) is faster than the step (a).
TO

BIMLA

WHO IS NO MORE
CONTENTS

Introduction 1
The Properties of Methylene 2

The Chemistry of Methylene and other Biradicals:
  Insertion Reaction 7
  Displacement Reaction 14
  Addition Reaction 15
The Monoradical Reaction of Biradicals 22
Abstraction Reaction of Biradicals 24
Aims of the present Research 26

EXPERIMENTAL

Chapter 1
  The Materials 27
  The Apparatus and Procedure 30
  The Columns 32
  Detector 35
  Calibrations 36

Chapter 2
  Attack of Methylene on MeOME 39

Chapter 3
  Methylene Reactions with Diethyl Ether 42
    Insertion Reaction 43
    Displacement Reaction 46
Chapter 3 continued

Abstraction Reactions 47
The Oxygenated Products 48 (Identification etc.)
Change in yields of 52

Chapter 4

Reactions of \( \text{CH}_2 \) with \( \text{EtOPr}^n \) 55
(Insertion Displacement and Abstraction)

Chapter 5

Reactions of \( \text{CH}_2 \) with \( \text{Pr}_1^i \text{OPr}^i \) 59
Insertion Reaction 60
Displacement Reaction 61
Abstraction Reaction 62
The Analysis of Lower Hydrocarbons 64
Temperature Dependence of Abstraction Reaction 65
Effect of Added Gases 66

Chapter 6

Discussion 69
Insertion Reaction 69
Displacement Reaction 71
Abstraction Reactions 74
Possible Mechanism 75
The Lower Hydrocarbons 78
Reactive Gases 80
The Mechanism of Ester Formation 81
Some suggestions for future work 85
ACKNOWLEDGEMENT

I wish to thank Dr. A.F. Trotman-Dickenson for much help and guidance. My sincere thanks are also due to Professor J.P. Kendall, Professor E.L. Hirst and Professor T.L. Cottrell for providing facilities and encouragement in the pursuit of this research. A special word of appreciation for Professor T.L. Cottrell, Dr. M. Ritchie and Dr. J.H. Knox for their inimitable method of teaching their courses that I attended. My sincere thanks are due to Dr. J.H. Knox whose helpful comments on the manuscript and expert knowledge in gas chromatography have all along been a source of great education and inspiration.

It is a pleasure to acknowledge the financial support given me by the Shell Oil group in whose subsidiary the author had once been associated fifteen years ago. Without their continued support and interest this research would have been difficult to accomplish, if not impossible.
The research reported in this thesis pertains to the reactions of methylene with ethers in gas phase. Methylene is generally considered to be the simplest example of the class of compounds known as biradicals, and in this introduction is given the evidence for its existence and a comparison of its chemistry with that of related biradicals.

By a simple and unambiguous definition a monoradical can be defined as a neutral molecule which has one unpaired electron and which is therefore paramagnetic. The corresponding definition of a biradical is a neutral molecule which has two unpaired electrons and which is paramagnetic. Spectroscopically a biradical will be in a triplet state if a double bond structure coupling the two electrons is geometrically possible. This definition must be used with caution, however, because there are molecules which from their method of preparation and their chemical reactivity might be expected to have two unpaired electrons and be in the triplet state, but which are in fact in the singlet state. For example, the nature of the ground state of methylene itself has not been definitely established and there is some evidence\textsuperscript{1,3,44} that it is singlet and does not contain unpaired electrons. On the other hand, there is no doubt that the ground state of the oxygen molecule, which behaves chemically as a biradical, is the triplet one; moreover, no reasonable electronic structure of trimethylene which does not involve two unpaired electrons
can be written. There is also the possibility for any given molecule that the singlet and triplet states are not greatly separated energetically, and therefore co-exist in appreciable concentration. This, though likely to be rare, may be true for methylene and is certainly so for some aromatic compounds such as the forms I and II, of p-xylylene,

\[
\begin{align*}
\text{I} & \quad \text{CH}_2 = \quad = \quad \text{CH}_2, \\
\text{II} & \quad \cdot\text{CH}_2 - \quad - \quad \cdot\text{CH}_2
\end{align*}
\]

which show both radical-like and non-radical like behaviour. In the following we shall use the term biradical for compounds which show a radical-like reactivity, without necessarily implying that the ground state is triplet.

As with the monoradicals, direct evidence for the existence of simple biradicals such as :CH$_2$ was not forthcoming until the Paneth\textsuperscript{4} mirror technique for the detection of free radicals in the gas phase was invented. Once this direct evidence was obtained, it became possible to postulate their existence in chemical reactions with more confidence and the great bulk of the evidence for the simple biradicals comes from kinetic and analytical evidence about reactions in which they are supposed to take part. In more recent years, spectroscopic and mass-spectrometric evidence for the existence of these radicals has become available, and all these sources of information will be used in the following survey to supplement where necessary the discussion of radical chemistry with which it is primarily concerned. In the first place we deal with the chemistry of methylene.

The Properties of Methylene

The existence of methylene has often been postulated to account for the kinetic and analytical data on hydrocarbon decomposition\textsuperscript{5}, oxidation\textsuperscript{6},
Rice demonstrated the existence of methylene on decomposing diazomethane at a temperature below 500°C, by identifying telluroformaldehyde as a product from tellurium mirror. It was shown that CH₂ group reacts with certain metals, viz., Te, Se, As and Sb but not with Zn, Cd, Hg, Tl, Pb, or Bi. The Me group on the other hand was found to react with all the metals listed above. Thus the formation of formaldehydes from Te, Se, As and Sb mirror provide a simple and conclusive test to distinguish whether methylene or methyl radicals are formed. The free radicals also react with non-metals like sulphur and iodine. Thus Belchetz and Rideal detected the presence of CH₂ by reaction with iodine to give methylene iodide in the heterogeneous decomposition of methane and ethylene on carbon and platinum filaments but no evidence for its formation in the homogeneous pyrolysis of methane at 1200°C was found. Methylene has also been detected by its reaction with a tellurium mirror, after a high frequency discharge was passed through ethylene, 1,1-dibromoethane and dioxane.

However, the main method of preparing methylene to study its reaction is by the photolysis of ketene in the gas phase or by thermal decomposition or photolysis of diazomethane either in solution or in gas phase. Ketene polymerises slowly at room temperature but can be preserved at liquid nitrogen temperature for long periods. It is therefore a more convenient source of methylene than is diazomethane, which is both poisonous and dangerously explosive, although Frey has recently worked out methods of dealing safely with the latter.

The absorption spectrum of ketene has long wave limit between 2600 and 3900 Å. At \( \lambda = 3850 \) Å, for example, the quanta absorbed
corresponds to 74 kcal, such that effective decomposition of ketene occurs. The photolysis of ketene have been studied by many workers who found that the main products were carbon monoxide and ethylene in the molar ratio 2:1. A detailed study made by Strachen and Noyes reveals the complexity of the photolytic decomposition. A discussion of the mechanism of the reaction must take into account the following facts:

(i) The quantum yield (of ethylene) increases with wavelength of light source but is independent of the percentage decomposition of the ketene.

(ii) The molar ratio of carbon monoxide to ethylene is slightly greater than 2:1.

(iii) Methylene reacts with carbon monoxide to give ketene.

(iv) The reaction probability of methylene with ketene is at least $10^{-2}$ times the collision probability.

(v) Higher hydro-carbons and traces of compounds containing the carbonyl group are produced.

Various reaction mechanisms to account for these facts have been proposed, and it appears that, though the primary reaction is simple, the secondary reactions are not clearly understood. According to one scheme the major reactions are:

1. $\text{CH}_2\text{CO} \xrightarrow{hv} \text{CH}_2\text{CO}^* \rightarrow \text{CH}_2 + \text{CO}$
2. $\text{CH}_2\text{CO}^* \rightarrow \text{CH}_2 + \text{CO}$
3. $\text{CH}_2^* + \text{CH}_2\text{CO} \rightarrow -\text{CH}_2\text{CH}_2\text{CO}$ or $-\text{CH}_2\text{COCH}_2$
4. $\text{CH}_2 + \text{CH}_2\text{CO} \rightarrow \text{C}_2\text{H}_4 + \text{CO}$
5. $\text{C}_2\text{H}_4 + \text{CH}_2^* \rightarrow -\text{CH}_2\text{CH}_2\text{CH}_2$
6. $\text{M} + -\text{CH}_2\text{CH}_2\text{CO} \rightarrow \text{M} + \text{C}_2\text{H}_4 + \text{CO}$
Steps (3) and (8) have also been postulated by Strachan and Noyes to account for the ratio CO/C2H4 being greater than 2:1 and for the formation of compounds of higher molecular weight. The formation of biradicals by step (3) is believed to arise from the breaking of any one of the three C-C bonds of cyclopropane intermediate assumed to be formed – the ratio of -CH2CH2CO to -CH2COCH2- being 2:1. The former may be assumed to decompose rapidly into C2H4 and CO while the latter is expected to be long-lived and could therefore account for some anomalous observations on the life of methylene mentioned in the next paragraph.

The quoted half-lives of methylene from different sources vary over a wide range with ketene and diazomethane respectively as sources of methylene, the half-lives as determined by mirror removal were 50 × 10^{-3} and 5 × 10^{-3} sec. respectively. Mirror removal here may have been due to relatively long-lived adducts of methylene with the parent molecules. The true life of methylene is likely to be much less. A short lifetime would be expected for a small biradical, and where much longer lifetimes have been reported as for CS, it seems unlikely that the molecule can reasonably be regarded as a biradical at all. Certainly, the ground state of CS seems to be a singlet.

The possible reactions of radicals are governed by their thermochemistry, and it would therefore be useful to know the heat of formation of methylene. This cannot be determined directly, but it is expected to
be large because it is formed by breaking two normal bonds. The heat of formation of the methyl radical is reliably known so that if \( D(CH_2-H) \) were known, \( H_f(CH_2) \) would follow directly. We have

\[
\Delta H_f(CH_2) = \Delta H_f(CH_3) + D(CH_2-H) - \Delta H_f(H)
\]

\[
= D(CH_2-H) - 20 \text{ kcal.}
\]

Unfortunately, \( D(CH_2-H) \) has not been reliably established but if methylene can abstract primary hydrogen atoms from alkanes it would, in the absence of a possible contribution to the energy from "hot" methylene molecules, imply \( D(CH_2-H) \geq 101 \text{ kcal} \), or \( \triangle H_f(CH_2) \geq 81 \text{ kcal} \). Frey\(^{22} \) has, following such an argument, taken \( \triangle H_f(CH_2) = 84 \text{ kcal} \). On the other hand, Hippie and Stevenson\(^{27} \) have determined \( D(CH_2-H) \) to be \( 3.7 \pm 0.3 \text{ kcal} \) from their interpretation of electron impact studies on methane which would mean a value of about 66 kcal for \( \triangle H_f(CH_2) \). Their interpretation of the electron impact measurements is, however, inconsistent with the now accepted 'high' value for the latent heat of sublimation of carbon, and may therefore be rejected.

The long wavelength limit for the photolysis of ketene itself, together with the heat of formation of ketene leads to \( \triangle H_f(CH_2) = 92 \text{ kcal} \), which is appreciably higher than any of the other values suggested. This suggests that the methylene formed in the photolysis may be 'hot', that is, it may carry excess energy.

It seems likely therefore that \( \triangle H_f(CH_2) \) is somewhere between 70 and 90 kcal, and that it is probably formed 'hot' when studied photochemically from either ketene or diazomethane. The energies of activation for its reactions with a large number of compounds are small and since
methylene is an extremely endothermic radical, molecules with very high degree of vibrational excitation result. As mentioned earlier the situation may be further complicated by the co-existence of singlet and triplet states of not very different energy so that it is not possible usefully to elaborate further the discussion of the thermochemistry.

The Chemistry of Methylene and other Biradicals.

The reactions of biradicals in general, and of methylene in particular, can conveniently be classified as reactions peculiar to biradicals and reactions typical of all radicals.

Reactions peculiar to biradicals may further be classified into:

1. Insertion reactions, such as
   \[ \text{CH}_2 + \text{C}_2\text{H}_6 \rightarrow \text{C}_2\text{H}_8 \]

2. Displacement reactions in which methylene displaces an olefin from a normal molecule; for example,
   \[ \text{CH}_2 + \text{C}_2\text{H}_5\text{OC}_2\text{H}_5 \rightarrow \text{CH}_3\text{OC}_2\text{H}_5 + \text{C}_2\text{H}_4 \]

3. Addition reactions in which methylene adds on to a double bond to form a cyclopropane derivative; for example,
   \[ \text{CH}_2 + \text{CH}_3 \text{CH} = \text{CH}_2 \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3 \]

4. Isomerization reactions in which a biradical is converted to an olefin are generally possible although not so for methylene itself. A typical possibility is
   \[ \text{CHCH}_3 \rightarrow \text{C}_2\text{H}_4 \]

These reactions will be discussed in detail before reactions common to all radicals are dealt with.

1. Insertion Reactions

In their preliminary work on the photolysis of diazomethane in
solution in diethyl ether, Maerwein, Rathjen and Werner showed that ethyl n-propyl and ethyl isopropyl ethers were formed, that is, that a CH₂ group had been inserted into C-H bond in the molecule. They also showed that in tetrahydrofuran solution, photolysed diazomethane gave rise to α and β-methyl tetrahydrofuran. The question arises as to whether insertion takes place directly into the C-H bond, or by way of an "ylid" in which the methylene reacts with the lone pair of electrons of the oxygen, and then migrates. This would mean insertion into C-O bond of the ether occurs. In a re-examination of the reaction Doering and co-workers studied the photochemical decomposition of diazomethane in furan in the hope that oxygen of the latter would permit the operation of "ylid" mechanism. No evidence for the formation of tetrahydropyran and therefore of ring-widening was found even by using the improved analytical technique (GLPC) which clearly argues against the "ylid" mechanism.

The first insertion of methylene to be studied in the gas phase was the formation of ethane from methane. The source of methylene was photolysed ketene which in the presence of methane gave ethane as the major product. The insertion reaction of methylene with higher hydrocarbons were first studied in solution and here the question arises of whether insertion takes place into C-O or C-H bond. However, the former possibility has been eliminated by the observation that ring-widening in cyclopropane, cyclopentane, and tetrahydrofuran does not occur. The photolysis of diazomethane in n-pentane solution gave yields of n-hexane, 2-methylpentane, and 3-methylpentane in proportion that corresponded exactly to the equal rates of attack on primary and secondary C-H bonds.
The gas phase photolysis of ketene in the presence of alkanes\(^2\) has given results shown in Table I which are in substantial agreement with relative rate ratios of the products from the first two reactants also done by Frey and Kistiakowsky\(^2\). They studied the reactions at room temperature within wide limits of pressure. The rate ratios seemed to be almost independent of pressure and the degree of decomposition of ketene. Assuming that a break in the C-C bond were taking place because of the high exothermicity of the reaction, it would have caused a number of reactions in the hydrocarbon molecule, thereby altering the rate ratios. The constancy of the values is yet another proof that insertion of CH\(_2\) into C-H alone occurs and not in C-C bond. From the Table I below, values for \(k_1/k_2\) have been calculated from the relative A factors and activation energy difference \((E_2-E_1)\). From Frey and Kistiakowsky's (loc. cit) work, the average value for the lower range of pressure is shown below for comparison. Taking the typical reactions

\[
\begin{align*}
\text{CH}_2 + \text{C}_2\text{H}_6 & \xrightarrow{k_1} \text{n-C}_4\text{H}_{10} \\
\text{CH}_2 + \text{C}_3\text{H}_8 & \xrightarrow{k_2} \text{iso-C}_4\text{H}_{10}
\end{align*}
\]

the values were:

<table>
<thead>
<tr>
<th>Reactant</th>
<th>Propene</th>
<th>Butane</th>
</tr>
</thead>
<tbody>
<tr>
<td>(k_1/k_2)</td>
<td>2.0</td>
<td>1.1</td>
</tr>
<tr>
<td>(k_1/k_2)</td>
<td>1.8</td>
<td>1.1</td>
</tr>
</tbody>
</table>

Agreement in the two sets of experiments is good.
**TABLE I**

The Reactions of Methylene with Alkanes

Typical Reaction: \( \text{CH}_2 + \text{C}_3\text{H}_8 \rightarrow n\text{C}_4\text{H}_{10} \quad \cdots \cdots (1) \)

\[ \rightarrow i\text{C}_4\text{H}_{10} \quad \cdots \cdots (2) \]

<table>
<thead>
<tr>
<th>Reactant</th>
<th>Product 1</th>
<th>Product 2</th>
<th>( A_1/A_2 )</th>
<th>( E_1-E_2 ) (cal/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{C}_3\text{H}_8 )</td>
<td>( n\text{C}<em>4\text{H}</em>{10} )</td>
<td>iso-( \text{C}<em>4\text{H}</em>{10} )</td>
<td>1.8</td>
<td>-70 ± 10</td>
</tr>
<tr>
<td>( \text{n-}\text{C}<em>4\text{H}</em>{10} )</td>
<td>( \text{n-}\text{C}<em>5\text{H}</em>{12} )</td>
<td>iso-( \text{C}<em>5\text{H}</em>{12} )</td>
<td>0.7</td>
<td>-260 ± 30</td>
</tr>
<tr>
<td>( \text{n-}\text{C}<em>3\text{H}</em>{12} )</td>
<td>( \text{n-6}\text{H}_{14} )</td>
<td>2 ( \text{Me-}\text{C}<em>5\text{H}</em>{12} )</td>
<td>0.7</td>
<td>-200 ± 50</td>
</tr>
<tr>
<td>( \text{n-}\text{C}<em>6\text{H}</em>{14} )</td>
<td>( \text{n-6}\text{H}_{14} )</td>
<td>3 ( \text{Me-}\text{C}<em>5\text{H}</em>{12} )</td>
<td>1.3</td>
<td>-350 ± 50</td>
</tr>
<tr>
<td>iso-( \text{C}<em>4\text{H}</em>{10} )</td>
<td>iso-( \text{C}<em>5\text{H}</em>{12} )</td>
<td>neo-( \text{C}<em>5\text{H}</em>{12} )</td>
<td>1.3</td>
<td>-190 ± 30</td>
</tr>
</tbody>
</table>

Some of the products were probably formed by the combination of alkyl radicals derived from H-abstraction by methylene. These reactions may be suppressed by the addition of a small amount of oxygen to the system. There are small differences in the activation energies for attack on different positions in the same molecule and these show an unexpected trend, attack on primary C-H having a lower activation energy than attack on secondary C-H. The figures for isobutane require further checking and it may be that all the deviation of the products from the statistical distribution is due to abstraction reactions. Knox and Trotman-Dickenson have attempted to calculate the relative A factors for the attack of CH\(_2\) on a number of alkanes by transition state theory assuming
that the activated complex has the form

\[
\text{CH}_2 \quad \text{CH}_3-\text{C} \quad \text{H} \\
\text{H}_2
\]

but did not obtain agreement with experiment. The model drawn was presumably oversimplified but the direction in which improvement with experiment should be sought is not obvious.

We now return to the insertion of CH₂ into compounds other than hydrocarbons. The original investigation of its reactions with ethers, mentioned above, has been repeated²⁹ with more refined analytical technique. It was found that in contrast to reaction in alkane solution, methylene clearly discriminated between primary and secondary C-H bonds in diethyl ether, and between the \( \alpha \)- and \( \beta \)-positions in tetrahydrofuran. In the ether, attack on the secondary C-H bond was slightly favoured, the ratio of isopropyl ethyl ether to n-propyl ethyl ether being 0.80 instead of the statistical 0.67. In tetrahydrofuran about 20% more of the \( \alpha \)-methyl derivative than \( \beta \)-methyl derivative was formed.

The detailed mechanism of the reaction with diethyl ether and di n-butyl ether has been studied using methylene labelled with \(^{14}\text{C}\) by Franzen and Fikentscher³⁴

\[
\text{CH}_2 + \text{C}_2\text{H}_5-0-\text{C}-\text{C}-\text{H} \quad \rightarrow \quad \text{C}_2\text{H}_5-0-\text{C}-^{14}\text{C}-\text{H}
\]

They found that in the n-propyl ethyl ether formed, all the \(^{14}\text{C}\) was in the
The possibility of insertion of CH$_2$ into C-N bonds has been examined by reacting it with N-methylpyrrolidine$^{36}$. Here the products were $\alpha$- and $\beta$-NMe$_2$ pyrrolidine and N-ethyl pyrrolidine, all of which can be explained on the assumption of insertion into C-H. If any C-N insertion had taken place, N-methylpiperidine should have been formed. This was carefully looked for spectroscopically (because its elution time in chromatography was identical with N-ethyl pyrrolidine) but none was found. Thus it appears that C-N insertion does not take place.

Insertion of methylene into C-Hal bond, on the other hand, takes place easily, just as C-H $\rightarrow$ C-CH$_3$, similarly C-Hal $\rightarrow$ C-CH$_2$-Hal. These reactions have great preparative value, for example, conversion of ter-butyl chloride and ter-butyl bromide into neopentyl chloride and bromide respectively occurs readily$^{37}$. On statistical considerations the expected ratio of the products of reaction

$$\text{CH}_3\text{CHCl}_2\text{CH}_3 + \text{CH}_2 \rightarrow \text{CH}_3\text{CHCl}_2\text{CH}_2\text{CH}_3,$$

$$\text{I} \quad + \quad (\text{CH}_3)_2\text{CHCH}_2\text{Cl}^+, \quad + \quad (\text{CH}_3)_3\text{C}_2\text{Cl}^-,$$

$$\text{II} \quad \text{III}$$

I, II, III are 6:1:1. Chromatographic analyses showed that isobutyl
chloride (III) was about \( \frac{1}{10} \)th of the I. Though the peaks for product I and II were not neatly separated, the latter has been estimated to be in higher proportion. One may thus conclude that there is a clear preference of attack on C-Cl compared to C-H bond and this is due to the electronegativity of halogen atom. Thus the hydrogen of -CHCl-
group is not easily substituted by methylene.

It is interesting to compare the insertion reactions of methylene with those of carbethoxycarbene CHCOOEt. This species is formed by the photochemical decomposition of diazoeacetic ester. In saturated hydrocarbon solution the carbethoxycarbene inserts into the C-H bonds giving saturated esters in good yield (as high as 50\%). This reaction is general and may be written as:

\[
\begin{align*}
N_2\text{CHCOOR}_1 & \longrightarrow \text{CHCOOR}_1 + N_2 \\
\text{HCOOR}_1 + \text{R}_2\text{H} & \longrightarrow \text{R}_2\text{CH}_2\text{COOR}_1
\end{align*}
\]

A typical example is the formation of ethyl cyclohexyl acetate by irradiation of ethyl diazoacetate in solution in cyclohexane. The same reaction takes place in a sealed tube at 150\(^\circ\) \(^{39}\). In the presence of copper powder, however, addition of ethyl diazoacetate to refluxing cyclohexane gave ethyl fumarate, clearly the product of dimerisation of carbethoxycarbene. Carbethoxy carbene produced under these conditions must therefore be insufficiently reactive to give the insertion reaction, although it can add to a double bond of cyclohexene to give a norcarane (bicyclo 4.1.0 heptane). These will be discussed under addition reactions.

With triethylamine, carbethoxycarbene gave \( \beta \) - and \( \gamma \)-diethyl-
aminobutyric esters - products of insertion reaction \(^{36}\). It was found that
the insertion of carbene into C-H on \( \alpha \) carbon to nitrogen was more than on \( \beta \). The reasonable explanation is that the electrophilic nature of carbene involves resonance in the intermediate complex.

There is some evidence that carbethoxy carbene can insert into C-O bonds by the "ylid" mechanism. Examples are to be found in its reactions with cyclohexanone and acetone in which enol ethers are formed\(^4\) as also in the ring-widening reactions in 1,3-dioxolane which gets converted into a p-dioxane\(^1\).

2. Displacement Reactions

In the displacement reaction a biradical displaces an olefin from a normal molecule. The first indication that this could happen was obtained from the decomposition of ethyl diazoacetate in various ethers\(^2\).

The reaction of carbethoxy carbene produced in this way with di-n-butyl ether gave ethyl butoxy acetate and but-1-ene as products. Similarly ethoxy, and propoxy benzene were converted into methyl phenoxy acetate and ethyl phenoxyacetate. On the other hand similar displacement reactions of methylene do not appear to take place in solution. When diazomethane was photolysed in solution of di-n-butyl ether, no methyl n-butyl ether or but-1-ene was found in agreement with an earlier report\(^1\).

The displacement reaction of methylene (generated from ketene) with ethers does take place in gas phase, however, as has been discovered in the investigation reported in this thesis.

A further recently reported biradical displacement reaction also concerns carbethoxy carbene rather than methylene: this time displacing ethylene from triethylamine\(^6\).
The mechanisms of these remarkable reactions are not known with certainty. It might be thought that an insertion first occurred followed by elimination of an olefin from the excited intermediate by a molecular reaction similar to the decomposition of tert-butyl bromide into isobutene and hydrogen bromide but such a mechanism seems less likely in solutions.

3. Addition Reactions

Carbon containing biradicals species are known to add to double bonds in olefin. These reactions are important for preparative purposes as well as for the additional evidence they provide for the existence of the biradicals taking part. All evidence indicates that carbenes add directly across double bonds to yield cyclopropanes. The reactions are highly exothermic. The addition reactions of methylene derived photo-chemically from diazomethane with cis and trans butene-2 have been much studied. The cis and trans cyclopropane derivatives are formed possessing enough energy to isomerize unless stabilized by collisional deactivation. The isomerization is responsible for the bulk of the products where both structural and geometric isomerization takes place. Consequently the true nature of even the simplest of the reaction, viz. addition of methylene to ethylene, was not recognised when it was first studied. A determined search for cyclopropane was only made after substituted cyclopropanes had been produced by the reaction of dichlorocarbenes with olefins in solution.

Frey and Kistiakovsky comprehensively studied the reactions of methylene with ethylene and the subsequent isomerization of the cyclopropane. The initial addition is some 84 kcal mole$^{-1}$ exothermic and the
cyclopropane so formed may readily isomerize to propene unless the pressure is high for deactivation to occur. The activation energy for the thermal isomerization of cyclopropane to propene is only 45 kcal mole\(^{-1}\). At a total pressure of 100 mm, most of the molecules isomerize, at 2000 mm few of them do. The nature of collisional deactivation is not clearly understood. It appears that the synthetic molecules have about one eightieth of the lifetime of an average thermally activated molecule. Even at highest pressures about half as much propene as cyclopropane was formed. Clearly insertion reaction is taking place whereby propene is directly formed. Addition of large quantities of carbon dioxide to the system (\(\text{CO}_2\) is not truly inert gas\(^{49}\)) resulted in larger yield of cyclopropane. It is possible that vibrational excitation of \(\text{CH}_2\) favours the insertion rather than the addition reactions of methylene.

The reaction of methylene with propene yields an activated methyl cyclopropane molecule\(^{31}\) which isomerizes to butene. The same molecule but with a different energy content, owing to the exothermicity of the reaction, may be formed by the insertion reaction of methylene with cyclopropane. These reactions have recently been examined by Butler and Kistiakowsky\(^{50}\). The lifetime of the energy-rich \(\text{Me}-\text{cyclopropane}\) depends largely on the source of \(\text{CH}_2\) as also on the choice between cyclopropane and propylene. In the former the \(\text{Me}-\text{cyclopropane}\) will have most of the vibrational energy in \(\text{CH}_3\) group. The findings that the composition of butenes formed does not depend on whether \(\text{CH}_2\) reacts with cyclopropane or propene means that the energy of the "hot" molecule flows freely among the normal modes of vibration of \(\text{Me}-\text{cyclopropane}\) in between the time of their formation and isomerization. As would be expected,
deactivation of complex molecules occurs at relatively lower pressures of gas. Only about 400 mm pressure is required to deactivate the cyclopropane compared to about 50 mm pressure required to stabilize "hot" dimethyl-cyclopropane produced from addition reaction of \( \text{CH}_2 \) with isobutene\(^{51} \). At room temperature addition reaction is several times faster than the insertion reaction. This is true of reactions of \( \text{CBr}_2 \) with olefins studied by Skell and Garner\(^{56} \) who also showed that these are more selective than those of methylene.

The "hot" Me-cyclopropane, referred to above, when produced from propene or cyclopropane, possesses different amounts of energy due to the fact that the transition states involved are different. Same compound of still different energy content can presumably be produced from ethyldiene and ethylene. Thus an experimental approach to test the theories of unimolecular reactions is available because compounds in excited state with definite amounts of energy distributed in a specific way are formed\(^{52} \).

The reaction of methylene with ketene which, in the gas phase, ultimately yields ethylene and carbon monoxide is likely to be an addition reaction\(^{23} \). Cyclopropanone is almost certainly formed first. The compound has not been isolated but the further reaction of methylene in solution yields cyclobutanone\(^{53} \). The work was consistent with earlier findings of Lipp and Koster\(^ {54} \) that at -70°C the following reactions occur:

\[
\begin{align*}
\text{CH}_2\text{CO} + \text{CH}_2\text{N}_2 & \rightarrow \text{N}_2 + \text{N}_2 + \downarrow = 0 \\
\downarrow = 0 + \text{CH}_2\text{N}_2 & \rightarrow \text{N}_2 + \downarrow \text{CH}_2
\end{align*}
\]

The criticism based on the fact that cyclobutanone at -70°C does not give
addition reaction\(^5\) could be explained on the basis of greater angle strain in cyclopropane than in cyclobutanone. It is estimated that the reaction of methylene with ketene will occur at every hundred collisions or less. Consequently the activation energy of this and all other reactions of methylene that can be studied when ketene is used as a source must be very low, not more than 1 or 2 kcal mole\(^{-1}\). It seems probable that the initial step in the reaction of methylene with carbon dioxide is also an addition reaction leading to the formation of carbon monoxide and formaldehyde\(^6\).

\[
\text{CH}_2 + \text{O} = \text{C} = \text{O} \rightarrow \left[ \begin{array}{c} \text{O} - \text{C} = \text{O} \\ \text{CH}_2 \end{array} \right] \rightarrow \text{HOHO} + \text{CO}
\]

Such a mode of attack with CH\(_2\) = C = O is suggestive of the formation of initial adduct which may itself be a reactive intermediate. If it will remove the tellurium mirrors then it may be the active agent in the mirror experiments of Norrish and Porter. The long lifetimes observed for these active agents could then be reconciled with the findings of Kistiakowsky and Kydd (loc.cit.).

It has been shown that the rate of attack of methylene depends little on the structure of the olefins\(^5\), though not much is known of the effect of substituents. On the other hand the reactivity of olefins towards CBr\(_2\)\(^5\) and still towards CCl\(_2\)\(^5\) depends distinctly on the structure of the unsaturated compound. The values found for the relative reactivities are given in Table II. A correlation has been established between these values and the relative rates for the reactions of Br\(^+\) and OH\(^+\) with olefins. Thus halocarbenes are electrophilic which finds further support from the work of Hâne and Dowell\(^5\) on CCl\(_2\) produced from chloroform by alkaline hydrolysis.
Its relative rates of reaction with Cl\(^-\), Br\(^-\), OH\(^-\) and I\(^-\) compared to water parallel their nucleophilicities.

**TABLE II**

<table>
<thead>
<tr>
<th>Olefin</th>
<th>log (rate of reaction relative to cyclohexane)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(\text{Cl}_2)</td>
</tr>
<tr>
<td>2,3-Dimethylbut-2-ene</td>
<td>1.73</td>
</tr>
<tr>
<td>2-Methylbut-2-ene</td>
<td>1.37</td>
</tr>
<tr>
<td>Isobutene</td>
<td>0.90</td>
</tr>
<tr>
<td>Cis-Pent-2-ene</td>
<td>0.33</td>
</tr>
<tr>
<td>Cyclohexene</td>
<td>0</td>
</tr>
<tr>
<td>Hex-1-ene</td>
<td>-0.73</td>
</tr>
<tr>
<td>Pent-1-ene</td>
<td>-0.86</td>
</tr>
</tbody>
</table>

The addition of a carbene to a cis-olefin has been found to yield only cis-substituted cyclopropane molecules. The studies on the relative rates of addition reactions of halocarbenes\(^{57, 56, 59}\) show clearly their electrophilic, non-free radical character. Both for methylene and halocarbenes stereospecific addition\(^{3, 44, 56}\) is suggestive of a three center rather than free radical type reaction. The possible structures for the attack of \(\text{Br}_2\) to cis and trans butene are

\[
\begin{align*}
\text{I} & \quad \begin{array}{c}
\text{C-C} \\
\text{\_\_}
\end{array} \\
\text{Br} & \quad \begin{array}{c}
\text{C-Br} \\
\text{\_\_}
\end{array} \\
\text{I} & \quad \begin{array}{c}
\text{C-C} \\
\text{\_\_}
\end{array} \\
\text{Br} & \quad \begin{array}{c}
\text{C-Br} \\
\text{\_\_}
\end{array}
\end{align*}
\]
If an intermediate of an open trimethylenetype I is formed it is unlikely that the configuration would be retained. Here I involves a propane bond angle such that C-C bond could cyclize with a half life $10^{-10}$ to $10^{-13}$ sec. Thus one would expect that an equilibration of diastereomeric radicals through rotation and inversion to be same if CCl$_3$ in place of iCCl$_2$ were the attacking radical. Indeed the relative reactivities of iCBr$_2$ and •CCl$_3$ towards a number of olefins did not show any correlation$^{56}$. It is possible that same factors do not apply to the rates of mono and biradical reaction. It is likely that a molecule in the triplet state would preferentially form an open intermediate of the form I. The addition reactions are stereospecific for CCl$_2$,$^{56, 57}$, CH$_2$,$^{44, 3}$ as also iCHCOOEt$^{59, 44}$ conforming to the form II which indicates these carbenes are in the singlet state. The extreme rapidity of the insertion reactions is a further argument in favour of this hypothesis$^{109}$. When methylene is inserted into an alkane both the reactant and the product are in the singlet states. If a change in multiplicity were involved, the reaction would be likely to be slow.

Additional support for this view comes from the study of the reaction of oxygen atoms with olefins$^{61-63}$. The photolysis of nitrogen dioxide by long wavelength light or mercury photosensitized decomposition of N$_2$O yield oxygen atoms in the triplet state provided the spin conservation rule holds. These atoms react with but-1-ene, forming addition products, butan-1-ol and butene oxide in about equal proportion. At short wavelengths the oxygen atoms are formed in the singlet first excited state. Under these conditions the yield of butene oxide is almost three times that of butyraldehyde. The latter could have formed directly in the
first case, whereas it is likely that with the singlet atoms it is a product of rearrangement of the oxide. There is another difference in the reactions of triplet oxygen to that of singlet methylene. The addition of oxygen atoms to substituted olefins yields mixed butene oxides

\[
\begin{align*}
\text{R}_1 \text{C} = \text{C} & \text{R}_2 \quad \text{O}^{3\text{F}} \quad \text{R}_1 \text{C} - \text{C} \quad \text{R}_3 \\
\text{R}_2 & \quad \text{R}_4
\end{align*}
\]

and not the stereospecific addition product, viz. cis-compound exclusively. These mixed butene oxides are a result of highly exothermic process. The oxygen atom forming two biradical ends combine to form three-membered ring. There must be a time lag between the opening and closing of the ring such that internal rotation becomes possible to give rise to trans product from cis and various other rearranged products indicated in the general form above.

The addition reaction of methylenes to aromatics like benzene and cyclohexylbenzene have also been shown to occur (Doering 1950-53). Thus \( \text{CH}_2 \) adds to the 'double' bond of benzene

\[
\begin{align*}
\text{C} & + \text{CH}_2 \rightarrow \text{I} \\
\text{II}
\end{align*}
\]

to give norcaradiene (II) which isomerises to give cycloheptatriene (I). Cyclohexyl tropilidine is the product obtained from cyclohexyl benzene in the same way. A large number of tropilidines have been prepared by photolysis of diazomethane in substituted benzene thus affording an
excellent method for ring-enlargement in a cyclic compound. The simplest example is of benzene ring-enlargement given above. Tropolidene (C₇H₈) is

\[ \text{C}_6\text{H}_6 + \text{CH}_2 \rightarrow \text{C}_7\text{H}_8 \xrightarrow{\text{KMnO}_4} \text{C}_7\text{H}_6\text{O}_2 \]

easily converted to tropolone by the oxidation of one ethylenic bond to a diketone grouping by KMnO₄, followed by alkali treatment converts it to tropolone anion. The final assignment of the structure of the tropilidene is based on conversion to pimelic acid or on u.v. spectrum – though it has not been definitely established.

Dichloro-carbene also adds to the double bond of cyclic compounds. Thus

\[ \text{C}_5\text{H}_5 \xrightarrow{\text{CCl}_2} \text{C}_7\text{H}_10 \xrightarrow{-\text{HCl}} \text{C}_7\text{H}_6\text{Cl} \]

Chlorobenzene is obtained from cyclopentadiene and where ring-widening is not possible due to high strain in the molecule as in CCl₂ attack on cycloheptatriene

\[ \text{C}_6\text{H}_6 \xrightarrow{\text{CCl}_2} \text{C}_7\text{H}_10 \xrightarrow{-\text{HCl} \text{130°}} \text{C}_7\text{H}_6\text{Cl} \]

1-chlorobenzocyclobutene was the product obtained and not chlorocyclooctatetraene II⁷⁸.
Reactions of methylene which are typical of all radicals could be divided into two classes -

(1) The Monoradical reactions of Biradicals.

(2) Abstraction reactions.

These comprise a somewhat unique property of methylene and some other biradicals to give reactions common to monoradicals.

(1) The Monoradical Reactions of Biradicals

Like methyl radicals, methylene reacts with metallic mirrors in a flow system. Thus Rice and co-worker found, as stated before, that the Te, Se, As, Sb mirrors were removed by methylene when diazomethane with ether or butane as carrier gas was passed through a tube at 550°C. When the temperature was raised to 660°C, however, CH₂ was converted into CH₃ and the resultant product from mirrors were dimethyl compound i.e. dimethyl ditelluride. The mirror removal by methylene is itself a monoradical property akin to the .CH₃ radicals as also the appearance of .CH₃ at 660°C as a result of H-abstraction which will be discussed later.

The only combination reactions of biradicals that are comparable with the monoradical reactions are the ring-closure reactions of poly-methylenes. The photolysis of cyclic ketones like cycloheptanone, -hexanone, and -heptanone possibly involve simultaneous rupture of two bonds joining the carbonyl group to give CO and a biradical. Where the formation of cyclic hydrocarbon is possible, as with five or six carbon atoms, this is readily formed; cyclopentanone on the other hand gave rise to isomeric butylene instead of cyclobutane. Blacet and Miller have determined the products of photolysis of ketones in detail. They found that cyclopentanone does give rise to cyclobutane while cyclobutanone gives cyclopropane and propylene, the latter being an isomerized product. In addition,
the other product being carbon monoxide and ethylene. The cyclization
process is exothermic by

\[
\begin{array}{c}
\text{HHHH} \\
\text{-C-C-C-} \\
\text{HHHH} \\
\text{CH}_2-\text{CH}_2 \\
\end{array}
\]

\[\Delta H = -54 \text{ kcal}\]

\[
\begin{array}{c}
\text{HHH} \\
\text{-C-C-} \\
\text{HHH} \\
\text{CH}_2-\text{CH}_2 \\
\text{CH}_2-\text{CH}_2 \\
\text{CH}_2 \\
\end{array}
\]

\[\Delta H = -52 \text{ kcal}\]

Since the activation energies for the decomposition and isomerization of
these cyclanes are only 60 and 65 kcal, it is possible that some of the
ethylene and propylene found in the products are formed by the reaction of
the activated cyclanes. The addition of inert gas should therefore result
into the collisional deactivation of the cyclanes (activated) with a
corresponding increase in their yield.

The dimerisation of methylene into C\textsubscript{2}H\textsubscript{4} is a doubtful issue.
The addition of CH\textsubscript{2} formed by the decomposition of CH\textsubscript{2}N\textsubscript{2} to CO yields
CH\textsubscript{2}CO\textsuperscript{76}. By using labelled carbon in CO, the reaction of CH\textsubscript{2} from ordinary
ketene yields\textsuperscript{77}

\[
\begin{align*}
\text{CH}_2\text{CO} & \xrightarrow{\text{hv}} \text{CH}_2 + \text{CO} \\
\text{CH}_2 + ^{13}\text{CO} & \rightarrow \text{CH}_2^{13}\text{CO}
\end{align*}
\]

These may be regarded as examples of methylene combination. The only
biradical dimerisation well established is that of acetylene to give
biacetylene\textsuperscript{69}. Ernest\textsuperscript{70} obtained ethylene derivatives under the
catalytic influence of copper powder. Thus

\[
\begin{align*}
\text{R',CO.CH}_2 + \text{R',CO.CH}_2 \xrightarrow{\text{Cu}} \text{R',CO.CH} = \text{CHCOR}^' + 2\text{N}_2
\end{align*}
\]
where \( R = \text{CH}_3 \) or \( \text{C}_2\text{H}_5 \). The rate of recombination was found to depend on the rate of carbene formation in the aromatic solvent used. The dimerisation of biradicals like diphenyl carbene does not occur either in liquid phase or in gas phase.\(^7\)

2. **Abstraction Reactions of Biradicals**

The best-established example of hydrogen abstraction by a biradical is the reaction of \( \text{CH}_2 \) with hydrogen studied by Gesser and Steacie.\(^7\) They found the following mechanism to fit into their kinetics:

\[
\begin{align*}
\text{CH}_2\text{CO} & \xrightarrow{\text{hv}} \text{CH}_2 + \text{CO} \quad \text{(1)} \\
\text{CH}_2 + \text{CH}_2\text{CO} & \rightarrow \text{C}_2\text{H}_4 + \text{CO} \quad \text{(2)} \\
\text{CH}_2 + \text{H}_2 & \rightarrow \cdot\text{CH}_3 + \text{H} \quad \text{(3)} \\
\text{H} + \text{CH}_2\text{CO} & \rightarrow \cdot\text{CH}_3 + \text{CO} \quad \text{(4)} \\
\cdot\text{CH}_3 + \cdot\text{CH}_3 & \rightarrow \text{C}_2\text{H}_6 \quad \text{(5)} \\
\text{CH}_3 + \text{H}_2 & \rightarrow \text{CH}_4 + \text{H} \quad \text{(6)}
\end{align*}
\]

Such a mechanism leads to a relationship:

\[
\frac{R_{\text{C}_2\text{H}_6}}{R_{\text{C}_2\text{H}_4}} = \frac{k_3[\text{H}_2]}{k_2[\text{CH}_2\text{CO}]}
\]

Experiments were done at \(-40^\circ\text{C}, 26^\circ\), and \(99^\circ\) and it was found that \( E_3 - E_2 = 0.8 \) kcal while \( E_6 = 10.2 \pm 0.5 \) kcal in excellent agreement with the previous work. At higher temperature reaction (6) leads to a chain reaction. The step (3) is very fast; the activation energy being about 0.8 kcal greater\(^7\) than for step (2), the latter having very small activation energy. In view of these we expect methylene to give hydrogen abstraction reaction with alkanes.

Irradiation of diazomethane in excess of carbon tetrachloride...
gave rise to a product of the form $\text{C(CH}_2\text{Cl)}_4$. A free radical mechanism involving the Cl-abstraction by methylene was postulated:

$$\text{CH}_2\text{N}_2 \rightarrow \text{CH}_2 + \text{N}_2 \quad \text{.........(1)}$$

$$\cdot\text{CH}_2 + \text{CCl}_4 \rightarrow \cdot\text{CH}_2\text{Cl} + \cdot\text{CCl}_3 \quad \text{.........(2)}$$

$$\cdot\text{CCl}_3 + \text{CH}_2\text{N}_2 \rightarrow \text{Cl}_3\text{OCH}_2 + \text{N}_2 \quad \text{.........(3)}$$

$$\text{CCl}_3\text{CH}_2 \rightarrow \text{CCl}_2\text{CH}_2\text{Cl} \quad \text{.........(4)}$$

The successive free radical rearrangement as in (4) (the 1,2 shifts of Cl) alternating with the reaction of $\cdot\text{CCl}_3$ with diazomethane (3) are some of the steps which have been suggested and can account for the formation of the end product $\text{C(CH}_2\text{Cl)}_4$.

Though the dimerisation of diphenyl carbene has neither been noted in gas nor in liquid phase, its hydrogen-abstraction distinguishes a monoradical behaviour. Thus for illustration:

$$\text{(C}_6\text{H}_5\text{)N}_2 \xrightarrow{\text{hv}} \text{C}_6\text{H}_5\text{C}: + \text{RH} \rightarrow \text{(C}_6\text{H}_5\text{)2 OH + R}$$

$$\xrightarrow{+\text{(C}_6\text{H}_5\text{)2 Cl}} \text{I} \quad \text{II} \quad \text{III}$$

The biradical I does not dimerise to IV, whereas the monoradical formed from it dimerises to tetraphenyldiethane (III). In addition, the biradical also reacts with the substrate to give a benzophenone azide. The proportion of the substituted ethane III formed depends entirely on the C-H bond strength of the solvent (RH) used. The OH and NH groups will also be converted into alkyl derivatives by the attack of phenyl carbene.
AIMS OF PRESENT RESEARCH

The reactions of methylene generated photochemically from keten were taken up to explore further their mode of attack in the light of reactions of biradicals. The view that different energy contents are responsible for the behaviour demands further inquiry. Methylene reactions with ethers were chosen because

(i) Doering's earlier report that :CH2 attacks 1, 2, 3 C-H bond with equal facility in the liquid phase demanded critical study in gas phase kinetics and the application of theory readily applicable to all hydrocarbons was sought.

(ii) The "Yld" mechanism so strongly supported by Meerwein and Huisgen was under controversy.

(iii) Monoradical reactions of methylene biradicals and their chain formation were intended to investigate.

(iv) The role of oxygen as a chain propagating agent was yet to be explored.

It was not known, for example, whether methylene gives a displacement reaction. This novel reaction was discovered by us in 1957. Nor was the H-abstraction in ethers ever reported before. Thus acetone, bi-isopropyl, acetaldehyde, ethane, butane etc. were found as a result of monoradical reactions.

Nothing was known about the role of oxygen. The addition of oxygen to the systems not only altered the course of reactions but resulted in the discovery of novel peroxy biradicals and monoradical which gave rise to large amounts of ethyl acetate and ethyl formate. Clearly these are a result of chain reactions. The details of these findings have been brought forward in these researches and were made possible by the advent of this extremely versatile analytical technique called gas chromatography.
CHAPTER 1

1.1. THE MATERIALS

Keten: - Keten can be obtained by the thermal decomposition of any compound containing the group CH$_2$CO; substances reported to have been used are acetone$^{79}$, acetic acid$^{80}$, ethyl acetate$^{81}$, and acetic anhydride$^{82,83}$. The impurities in keten so produced arise from the fact that keten reacts with the parent molecule, dimerises, and by-product gases are produced.

An apparatus similar to that used for the low-pressure pyrolysis of propionaldehyde which yields methyl keten$^{43}$ may be employed for the preparation of keten from acetic anhydride. Our apparatus, as modified, is shown in Fig.13. A is a 50-ml pyrex trap fitted with a glass-to-glass (B 14) joint to the tube L. A distilled fraction of acetic anhydride (139.6°C) was heated to boiling and oxygen-free nitrogen was blown through it. Direct distillation into A via stopper S, at reduced pressure, kept the acetic anhydride out of contact with moist air. A pyrex tube L leads into the reaction chamber Q, made of quartz tube about a meter long standing vertically in an electrically-heated furnace. The furnace temperature was maintained at about 500°C using an energy regulator. The tube L was kept at 140–150°C by spiral winding a resistance wire around it. A fine capillary at B was inserted to maintain low pressure on the product side thereby reducing the dimerisation of keten. The trap D contained dry ice-alcohol mixture and condensed out most of the undecomposed anhydride.

To start with, the liquid nitrogen dewar was kept on A and the system pumped down after which the dewar was replaced with warm water. In this way adequate amount of acetic anhydride entered the furnace and
decomposed into keten and acetic acid

\[(CH_3CO)_{2O} \rightarrow CH_2 = CO + CH_3COOH\]

in the molar ratio 1:1. The keten was condensed in trap T cooled in liquid nitrogen. From time to time the dewar on T was lowered to melt the frozen keten to free the passage through it. After an adequate amount of keten was collected further purification was carried out by bulb-to-bulb distillation. Evaporating from dry-ice trap temperature, the first 10\% of distillate and the last 20\% was rejected; the middle fraction was stored at liquid air temperature. The purity of keten used in the present work was always checked by chromatography where no trace of any other component was observed.

**Ethers.** Most of the ethers employed for experimental studies were prepared in the laboratory by the sulphuric acid method or by the reaction of an appropriate alkyl bromide with sodium alkoxide. Primary separation of ethers was carried out by fractional distillation. Only the middle fractions of the distillate were collected. Extensive use was made of the large-scale chromatography column specially installed for the purpose of purification. For reasons discussed under Displacement Reactions, care was always taken to ensure that the ethers were free of alcohols.

**Dimethyl Ethers.** 4.5 mls of conc sulphuric acid was gradually added to 20 mls methanol in a distillation flask and the mixture allowed to reflux on an oil bath at 140°C. By means of a dropping pipette more methanol was added at a rate at which methyl ether was collecting as gas. The sample thus obtained was distilled from a trap at -30 to a trap at -186°C at least twice giving ether of about 99.95\% purity.
Methyl Ethyl Ether. About 3 gms of freshly cut sodium metal was dissolved in about 30 mls of methyl alcohol, refluxed for about 2½ hrs. The excess of sodium metal was filtered off on glass wool and the clear solution vacuum dried. Ethyl bromide was then added drop by drop into sodium methoxide, refluxed under water-cooled condenser while maintaining the receiver at 0°C. Chromatographic purification was resorted to in order to separate out impurities.

Di-ethyl Ether. C.P. grade ether anaesthetic was used. It was dried with sodium and redistilled, only the middle fraction coming through at 34.6 being retained. This was found to be sufficiently pure by gas chromatography and infra-red analysis.

Ethyl n-propyl Ether. The method of preparation was the same as for methyl ethyl ether except that propyl bromide was reacted with sodium ethoxide. The ether was purified by two distillations and large scale chromatography. The large chromatography columns (6 meters long and 2 cm in diameter) contained Firebrick (52-72 mesh) supporting 20% di-nonyl phthalate and were heated to 80°C.

Ethyl iso-propyl Ether. Sodium ethoxide was reacted with iso-propyl bromide and the ether purified by large scale gas chromatography.

Di iso-propyl Ether. This was supplied by B.D.H. and contained about 0.5% ethyl isopropyl ether which was recovered by the large scale gas chromatography.
1.2. THE APPARATUS AND PROCEDURE

The kinetic apparatus employed in the present investigation is shown in Fig.1; Fig.2 shows the analytical section of the apparatus in somewhat greater detail.

Experiments were conducted in an all-glass high vacuum system which could be evacuated in 30 mins to better than $10^{-4}$ mm as checked by a vacuostat, by means of a mercury vapour diffusion pump backed by a rotary oil pump.

In making up reaction mixture, in which the ether was always present in excess, about 2 cm pressure of keten was first let in into the reaction vessel V from the storage trap D. Residual keten in the line was condensed back into D followed by closing tap R. The required pressure of ether (gas) was then allowed to build up from its storage bulb into the short line P&S and S opened. As about 5 cm (amount desired) Hg pressure of ether gas streamed through the capillary into V, adequate mixing took place in V. At the same time the chances of keten diffusing back were minimized. Trial tests had shown that opening S for just three seconds was adequate to stabilise the pressure on either side. Thus the pressure of ether let into V could be easily read. The remaining ether was condensed back into its bulb which was isolated before the apparatus was pumped out.

The irradiation source was by means of a 125 Watt Osram medium pressure mercury lamp whose unfiltered light was allowed to play on V. The outer glass bulb of the lamp cut off so that both the reaction vessel and the lamp could be conveniently placed parallel and housed in a cylindrical box made from polished aluminium foil. The lamp was operated direct from the
A.C. mains using choke and a capacitor. Before starting an irradiation, however, the lamp was allowed to warm up under an opaque black cover for about twenty minutes. During the subsequent timed irradiation about 20% of the keten was decomposed, and the products allowed to stand in V for a few minutes.

Keeping stopcocks Q, R, and S closed, a liquid air trap was kept around trap T. S was now opened and the products drawn out from V by the Toepler pump. Complete condensation was ensured by passing the gas several times back and forth into V. This procedure was necessary particularly when the mixture contained uncondensable gases like nitrogen and oxygen. Direct pumping out of the uncondensables via W and M tended to give erratic results due to incomplete condensation of more volatile condensables.

The uncondensables were pumped off, and the 'U' trap on the chromatography column having been evacuated to low pressures, was cooled by liquid oxygen transferring Dewar from T to 'U' and keeping W, S shut but M open. After allowing about ten minutes for distillation into 'U', N was also opened to the vacuum line for a short while if the vacuum on U was not standing low. At the relatively low working pressure the products were transferred adequately into U. With M and N shut, the cold trap was removed and the nitrogen supply directed via L, U, and N thus feeding the products into the chromatography system. U was warmed quickly with tap water to vaporise the products. A buffer volume preceding U was fitted and was large enough to take care of the abrupt change in nitrogen flow. This method when used either for the injection of a sample or for the calibration of the products gave symmetrical peaks on a chromatogram. If, however, the peaks showed tendency to tail off, the column packing was taken out and
re-tapped to remove 'cavities' which appeared as a result of continuously subjecting the column to sudden changes in flow of the carrier gas. Glass wool was preferred to cotton pads for the column ends to keep the packing in position and to reduce retention of the products on the pads.

The response of the thermal conductivity cells is nearly linear in the concentration of any single component, but the response may differ from one substance to another. According to some, it is proportional to the weight of the components, while others maintain it is proportional to the mole fraction. Here the calibration was carried out on the basis of mole fraction by employing a micro-burette which is essentially a modified McLeod gauge. It was capable of measuring gas volumes from 0.01 to 10 micromoles of lower boilers quite conveniently. By injecting small aliquots of any component below its saturated vapour pressure, it was possible to select a wide range of concentrations and in this way calibration graphs constructed for the individual products.

1.3.1. THE COLUMNS

Partition columns were used for the separation of lower and higher ethers formed by the attack of methylene on the ether under study. The other products like the aldehydes, ketones, and where oxygen was added to the system the esters formed, were also easily resolved on these columns. The adsorption columns were employed for the separation of lower hydrocarbons produced in the reactions. All tubing other than the packed column was capillary to reduce diffusion of the eluted constituents to the minimum.
Partition Columns

6 ft length of glass tubing (i.d. 3 mm and 4 mm) bent into the form of U, joined when necessary into the form W, were packed with Celite or Firebrick of a mesh size chosen to give the necessary number of theoretical plates. A set of columns containing stationary phase of different polarities were kept on hand which met the requirements of the changing composition and the nature of the products.

Celite (kieselguhr), size largely below 100 mesh, was purified by treating with dil HCl (50:50) for four hours and washed acid-free in a running stream of fresh water, finally given a washing with dil ammonia (5% v/v). It was baked in an air oven at 120°C for three hours, cooled, and the liquid phase was deposited and dried completely free of solvent. At a later stage of the work chromatography grade celite (80-100) was used. The liquid phase was deposited using the solvents given below in Table 1, which includes a list of packing employed in the present work.

**TABLE 1**

<table>
<thead>
<tr>
<th>Column 6 ft.</th>
<th>Celite</th>
<th>Liquid phase</th>
<th>Solvent used</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) 4-5 mm (i.d.)</td>
<td>100-120</td>
<td>20% Dinonyl phthalate</td>
<td>Acetone</td>
</tr>
<tr>
<td>(2) 2-3 mm</td>
<td>80-100</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>(3) &quot;</td>
<td>&quot;</td>
<td>20% Polyethylene glycol</td>
<td>CH₄OH</td>
</tr>
<tr>
<td>(4) &quot;</td>
<td>&quot;</td>
<td>Squalene</td>
<td>&quot;</td>
</tr>
<tr>
<td>(5) 4-5 mm</td>
<td>Firebrick 52-72 mesh</td>
<td>20% Dimethyl phthalate</td>
<td>Acetone</td>
</tr>
<tr>
<td>(6) &quot;</td>
<td>100-120</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>(7) &quot;</td>
<td>72-92</td>
<td>20% Dibutyl phthalate</td>
<td>&quot;</td>
</tr>
<tr>
<td>(8) &quot;</td>
<td>52-72</td>
<td>Nitrobenzene</td>
<td>&quot;</td>
</tr>
<tr>
<td>(9) &quot;</td>
<td>72-92</td>
<td>Silicone grease</td>
<td>Benzene</td>
</tr>
<tr>
<td>(10) &quot;</td>
<td>52-72</td>
<td>Di-octyl Phthalate</td>
<td>Acetone</td>
</tr>
</tbody>
</table>
Adsorption Columns

Chromatography grade Alumina (Spence) was sieved and then activated by roasting in a muffle at 450°C for three hours, then cooled down to a temperature of 150°C and transferred to a vacuum dessicator. In view of the fact asymmetric peaks were often obtained with alkanes, its activity was reduced by depositing 1-2% squalane or an ester (Table 2).

| Table 2 |
|------------------|------------------|------------------|------------------|
| Column dia.      | Mesh Size        | Liquid phase     | Solvent used     |
| (11) 4-5 mm.     | 40-60            | 1% squalane      | Petroleum ether  |
| (12)             | 32-100           | 2% "             | "                |
| (13)             | "                | 2% Dinonyl Phthalate | Acetone         |

Such a treatment of poisoning as in columns No. 11-14 gave excellent separation of hydrocarbons.

It being known from the retention volume measurements that the lower hydrocarbons were eluted extremely fast on partition columns, compared to other products in the mixture, the adsorption (alumina) column was connected in series to the partition (firebrick) column. The products of reaction collected in the 'U' were injected through these combined columns for a time period shorter than the retention volume of the first product to be eluted from the partition column. A 3-way tap connecting the two was then turned to isolate the alumina column, which now contained only the lower hydrocarbons, thereby allowing the analysis of the rest of the products to be completed on the partition column. The nitrogen flow was now directed back via the alumina column to elute the lower hydrocarbons. In this way
correlation of all the products obtained in the complete analysis was readily available under identical conditions.

The column temperature was controlled by an electrically heated jacket which consisted of an inner glass tube (dia 30 mm) wound with nichrome heating tape, the whole being placed in a thick fibre glass jacket supported horizontally on the frame of the apparatus. The current to the column jacket was supplied through a variac transformer. In this way the temperature of the column was controlled to within ±1°C.

1.3.2. DETECTOR

A katharometer was used as detector throughout the present work. The circuit (Fig.2) consisted of a balanced Wheatstone bridge incorporating two tungsten filaments (13 ohms each) stretched along the axis of two channels drilled in a brass block. The block was cylindrical piece (7.7 x 7.5 cm) with two channels, one for the balancing and the other as detecting side. It was housed in a thermally insulated box and had a high heat capacity so that small changes in the laboratory temperature did not appreciably alter its sensitivity or cause base line drift during analyses which took 2-3 hours.

Each filament formed an arm in the circuit to which current was supplied from a 4-volt battery. The battery current was controlled by a 10 A variable resistance V. With the flow rate of carrier gas (N₂) same, the zero point on the recorder pen was adjusted by R₃. Passage of an impurity (gas product) through the detecting side produced an off-balance current depending upon its thermal conductivity which was recorded on a strip chart on the 'continuous balance' lmV Honeywell-Brown recorder.
1.3.3. **CALIBRATIONS**

For the quantitative measurements of the products of reaction, it was necessary to carry out calibrations. This of course followed the analyses and the identification of each product of reaction but will be described here since the calibrations will be referred to in the text that follows. The problem was approached in different ways. Firstly, the products were combusted either in a copper furnace or in the combustion pipette, C, (Fig.1); secondly, by the method of internal normalization, and lastly, by the micro-burette method. These are discussed briefly as follows:

**The Combustion Method.**

A copper oxide furnace made out of a quartz tube (20 cm long, 6 mm i.d.), electrically heated, was fitted to the outlet end of the conductivity cell so that any of the product appearing on a chromatogram could be picked up for combustion. The carbon dioxide so formed was collected in a spiral trap filled with pyrex helices and frozen at liquid oxygen temperature. After collecting all the carbon dioxide formed from the component as indicated by the chromatogram, the trap was fitted on to the apparatus, degassed to remove nitrogen (carrier gas), and the carbon dioxide remaining at liquid oxygen temperature was transferred to the graduated Toepler volume for measurement. It was expected that in this way a correlation of carbon number of a component (measured as CO$_2$) with the peak areas on a chromatogram would be possible. But when actual samples were measured, combusted, and the CO$_2$ formed measured, the reproducibility was poor. A combustion pipette C, was then incorporated close to the Toepler volume where the eluted product, identified from its chromatogram,
was condensed out and after degassing as usual combusted on the platinum filament in C. Calculations invariably showed a source of discrepancy possibly due to too frequent contact with the grease of stoppers on the apparatus. It was thought that on using an excess of solvent, the loss of actual component could be reduced, hence internal normalization was tried.

**Internal Normalization**

Accurate mixtures of ether and n-pentane were made up and sample injected into trap D by a 1.0 ml syringe. The samples were then distilled into the U to ascertain the effect of stopcocks on the way. It was found that stopcock grease does reduce the reliability of values. However, the microburette mB (Fig.1) enabled absolute calibrations of ethers (gas) to be carried out without involving direct contact with grease and this procedure was therefore adopted.

**Microburette Method**

Gaseous samples were stored in 2-litre vessels, whereas liquid samples were kept in traps which are shown in Fig.1. The injection of sample into the column was carried out as follows: The sample was first degassed, after freezing it to liquid oxygen temperature. The system including the microburette (a modified McLeod gauge) was brought to low vacuum along with the U. U was now closed and an aliquot of a sample allowed to vaporise into the sealed end of mB. The level of mercury was raised by manipulating the 3-way tap S to a suitable mark at A, B, C. The rest of the system was pumped down again and a reading taken on the manometer. Care was always taken to draw an amount of sample into microburette which would be below its vapour pressure.
Peak areas (sq cm) were measured according to trapezoidal rule against which were plotted molar concentrations of the components and a set of graphs constructed. To bring the sensitivity to a normal basis, the peak areas corresponding to 3 micromoles of each fraction were recorded which were then converted to a uniform flow rate basis viz. 20 c.cs per minute (Table 3).

The abbreviations for the chromatography columns given in the same table correspond to the type of packing, the liquid phase present, and where the column length was a single 'U' (6 ft. length) it is marked S, while for double length (12 ft.) it is marked D. For example, C(80-100)(DNP)^S refers to a column with Celite packing carrying dinonyl phthalate and is half S length viz. 3 ft.

Depending upon whether the columns used were packed with firebrick, celite, or activated alumina either singly or in combination for the purpose of product analysis, only the corresponding values for the sensitivities from Table 3 were applied, the reason for doing so being that a plot of the calibration values (given in the last column of the Table 3) against carbon numbers of the compound did not fall on a single straight line. Instead, a greater slope for the sensitivities done on firebrick column compared to those done on celite column was obtained. Table 3 lists the sensitivities of almost all the compounds found as products of the reactions studied during the present work.
<table>
<thead>
<tr>
<th>No.</th>
<th>Compound</th>
<th>B.P. °C</th>
<th>Chromatography column</th>
<th>N₂ flow-rate</th>
<th>Area (sq.cm)</th>
<th>Converted to N₂ flows: 20 cc./mt</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2,3 di Me Butane</td>
<td>58.1</td>
<td>C(DNP) + Act.Al.</td>
<td>11</td>
<td>38.4</td>
<td>21.0</td>
</tr>
<tr>
<td>2</td>
<td>Propane</td>
<td>-42.1</td>
<td>F(DMP) S</td>
<td>25</td>
<td>2.43</td>
<td>3.0</td>
</tr>
<tr>
<td>3</td>
<td>Iso Butane</td>
<td>-11.3</td>
<td>C(DMP) + Act.Al.</td>
<td>11</td>
<td>8.1</td>
<td>8.1</td>
</tr>
<tr>
<td>4</td>
<td>Me O Et</td>
<td>7.9</td>
<td>F(DMP) D</td>
<td>20</td>
<td>6.42</td>
<td>6.4</td>
</tr>
<tr>
<td>5</td>
<td>CH₃CHO</td>
<td>21</td>
<td>&quot;</td>
<td>20</td>
<td>5.0</td>
<td>5.0</td>
</tr>
<tr>
<td>6</td>
<td>Et O Et</td>
<td>34.6</td>
<td>&quot;</td>
<td>20</td>
<td>7.56</td>
<td>8.70</td>
</tr>
<tr>
<td>7</td>
<td>Me O Prᵣₙ</td>
<td>39.1</td>
<td>&quot;</td>
<td>20</td>
<td>8.8</td>
<td>10.1</td>
</tr>
<tr>
<td>8</td>
<td>Et O Priᵣₙ</td>
<td>54</td>
<td>C(80-100) DNP₃S + C(80-100) sq.</td>
<td>21</td>
<td>18.4</td>
<td>18.4</td>
</tr>
<tr>
<td>9</td>
<td>Et O Priᵣₙ</td>
<td>64</td>
<td>&quot;</td>
<td>23</td>
<td>18-21°C (10.5)</td>
<td>12.1</td>
</tr>
<tr>
<td>10</td>
<td>Et O Priᵣₙ</td>
<td>64</td>
<td>F(DMP) D</td>
<td>23</td>
<td>18-21°C (10.5)</td>
<td>12.1</td>
</tr>
<tr>
<td>11</td>
<td>Et O Priᵣₙ</td>
<td>54</td>
<td>&quot;</td>
<td>23</td>
<td>&quot;</td>
<td>10.0</td>
</tr>
<tr>
<td>12</td>
<td>Priᵣiliate O Priᵣ</td>
<td>59</td>
<td>&quot;</td>
<td>23</td>
<td>&quot;</td>
<td>12.5</td>
</tr>
<tr>
<td>13</td>
<td>Priᵣₙ O Priᵣₙ</td>
<td>58</td>
<td>&quot;</td>
<td>23</td>
<td>&quot;</td>
<td>14.6</td>
</tr>
<tr>
<td>14</td>
<td>Et Formate</td>
<td>54</td>
<td>C(80-100) DNP₃S + C(80-100) (sq.) S</td>
<td>21</td>
<td>13.7</td>
<td>14.7</td>
</tr>
<tr>
<td>15</td>
<td>Et Acetate</td>
<td>77</td>
<td>&quot;</td>
<td>21</td>
<td>&quot;</td>
<td>22.4</td>
</tr>
<tr>
<td>16</td>
<td>Acetone</td>
<td>56.5</td>
<td>F(DMP) D</td>
<td>23</td>
<td>48-50°C (8.67)</td>
<td>9.96</td>
</tr>
<tr>
<td>17</td>
<td>C₂H₂CHO</td>
<td>50</td>
<td>C(DNP) S</td>
<td>20</td>
<td>8.84</td>
<td>8.8</td>
</tr>
<tr>
<td>18</td>
<td>Propane</td>
<td>38.5</td>
<td>C(DNP) + Act.Al.</td>
<td>35</td>
<td>3.5</td>
<td>3.2</td>
</tr>
<tr>
<td>19</td>
<td>Iso Butane</td>
<td>-11.3</td>
<td>&quot;</td>
<td>18.5</td>
<td>&quot;</td>
<td>9.3</td>
</tr>
<tr>
<td>20</td>
<td>Propylene</td>
<td>-47</td>
<td>&quot;</td>
<td>18-20°C</td>
<td>12.6</td>
<td>14.5 (calculated on EtOPrᵣₙ basis)</td>
</tr>
<tr>
<td>21</td>
<td>Et O Bu₁</td>
<td>81.1</td>
<td>&quot;</td>
<td>23.0</td>
<td>12.6</td>
<td>24.0</td>
</tr>
<tr>
<td>22</td>
<td>Et O Bu₂sec</td>
<td>81.2</td>
<td>value F(DMP) D</td>
<td>&quot;</td>
<td>&quot;</td>
<td>14.5</td>
</tr>
<tr>
<td>23</td>
<td>Et O Bu₃sec</td>
<td>92.3</td>
<td>&quot;</td>
<td>&quot;</td>
<td>14.0</td>
<td>16.1</td>
</tr>
<tr>
<td>24</td>
<td>Me O Priᵣₙ</td>
<td>32.5</td>
<td>F(DMP) D</td>
<td>&quot;</td>
<td>7.0</td>
<td>8.1</td>
</tr>
<tr>
<td>25</td>
<td>Priᵣiliate O Priᵣₙ</td>
<td>53</td>
<td>&quot;</td>
<td>&quot;</td>
<td>12.0</td>
<td>13.8</td>
</tr>
<tr>
<td>26</td>
<td>Priᵣ₂ o Bu¹</td>
<td>87.7</td>
<td>&quot;</td>
<td>&quot;</td>
<td>13.6</td>
<td>15.6</td>
</tr>
<tr>
<td>27</td>
<td>Priᵣ₂ o Bu</td>
<td>90</td>
<td>&quot;</td>
<td>&quot;</td>
<td>13.8</td>
<td>15.9</td>
</tr>
<tr>
<td>28</td>
<td>Acetone</td>
<td>56.5</td>
<td>C(DNP) S</td>
<td>20</td>
<td>10.2</td>
<td>10.2</td>
</tr>
</tbody>
</table>
CHAPTER 2

ATTACK OF METHYLENE ON DI-METHYL ETHER

Competitive rate measurements of the insertion reaction of methylene into the $^0_1$ C-H bonds of dimethyl and diethyl ethers were made. Insertion of CH$_2$ into the $^0_1$ C-H bonds of dimethyl ether gives methyl ethyl ether. The same reaction with diethyl ether gives ethyl n-propyl ether. Thus a comparison could be made of the efficiency of attack on the $^0_1$ C-H of the two ethers. Such an approach was dictated by the fact that the absolute concentration of methylene biradicals cannot be obtained.

Many of the difficulties disappear when measurements of relative rates of attack on any two ethers, R-O-R and R'-O-R' (by analogy, the competitive reactions of atoms and free radicals with hydrocarbons) are carried out. Competitive reactions of methylene with dimethyl and diethyl ether were therefore chosen which necessitated a prior knowledge of the relative rates of formation of MeOEt/EtOPr from diethyl ether alone. Although the latter experiments were done first, the reactions with dimethyl ether have been considered in this chapter to keep a sequence of lower to higher ethers in the discussion. In the presence of both dimethyl and diethyl ether, the following reactions occurred.

Insertion $\text{CH}_2 + \text{C}_2\text{H}_5\text{OC}_2\text{H}_5 \xrightarrow{k_1} \text{C}_2\text{H}_5\text{OCH}$\text{(CH}_3\text{)}_2$ 

Insertion $\text{CH}_2 + \text{C}_2\text{H}_5\text{OC}_2\text{H}_5 \xrightarrow{k_2} \text{C}_2\text{H}_5\text{OC}_2\text{H}_7$ 

Displacement $\text{CH}_2 + \text{C}_2\text{H}_5\text{OC}_2\text{H}_5 \xrightarrow{k_3} \text{CH}_3\text{OC}_2\text{H}_5 + \text{C}_2\text{H}_4$ 

Insertion $\text{CH}_2 + \text{CH}_3\text{OCH}_3 \xrightarrow{k_4} \text{CH}_3\text{OC}_2\text{H}_5$

Thus methyl ethyl ether arises by reaction (3) and (4) from both ethers. This scheme then gives the rate ratios
\[
\frac{R_{\text{MeOEt}}/R_{\text{EtOPr^n}}} = \frac{k_3}{k_2} + \frac{k_4}{k_2} \frac{[\text{MeOME}]}{[\text{EtOEt}]}
\]

At 100°C, values for the left hand side of equation are listed in column marked MeOEt (Table 2.1.). At corresponding temperature values for \(\frac{k_3}{k_2}\) may be taken from Table 3.1.2, where the average rate ratio for MeOEt/EtOPr^n formation from EtOEt alone was found to be 0.38. This has to be allowed for since the MeOEt also arises from EtOEt by a novel mode of reaction (a displacement reaction) discussed in Chapter 3. The ratios of the two ethers used are also given in the table below and by way of illustration let us consider Run 32 to calculate \(\frac{k_4}{k_2}\). Substituting the values in the aforementioned relationship we have,

\[
2.07 = 0.38 + \frac{k_4}{k_2} \times \frac{4.1}{4.0}
\]

whence \(\frac{k_4}{k_2} = 1.65\)

In this way values given in the last column of Table 2.1 were calculated and their molar averages found to be 1.72.

**TABLE 2.1.**

<table>
<thead>
<tr>
<th>Run No.</th>
<th>F from Keten</th>
<th>MeOME</th>
<th>EtOEt</th>
<th>Normalised to EtOPr^n</th>
<th>(k_4/k_2) (calc.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>32</td>
<td>1.0</td>
<td>4.1</td>
<td>4.0</td>
<td>2.07</td>
<td>1.58</td>
</tr>
<tr>
<td>37</td>
<td>1.0</td>
<td>8.0</td>
<td>4.6</td>
<td>3.16</td>
<td>1.91</td>
</tr>
<tr>
<td>56</td>
<td>2.0</td>
<td>8.0</td>
<td>4.0</td>
<td>3.77</td>
<td>1.76</td>
</tr>
<tr>
<td>54</td>
<td>1.0</td>
<td>4.0</td>
<td>2.0</td>
<td>3.85</td>
<td>1.64</td>
</tr>
<tr>
<td>58</td>
<td>2.0</td>
<td>8.0</td>
<td>4.0</td>
<td>4.24</td>
<td>1.77</td>
</tr>
<tr>
<td>41</td>
<td>0.5</td>
<td>3.0</td>
<td>1.0</td>
<td>5.48</td>
<td>1.79</td>
</tr>
</tbody>
</table>

Molar Average = 1.74 1.72
Since there are six primary C-H bonds available both in MeOMe and EtOEt, the results show that the efficiency of attack on primary C-H bond of the former is higher than that of the latter. Small quantities of acetaldehyde were also found as the product of the reaction of CH₂ with MeOMe by itself but it was not determined quantitatively.

Acetaldehyde could be formed either by way of direct molecular reaction via a somewhat complex transition state

\[
\text{CH}_2 + \text{MeOMe} \rightarrow \text{CH}_3\text{CHO} + \text{CH}_4
\]

It is unlikely to be the result of abstraction reaction to followed by a disproportionation of radical such as

\[
\text{CH}_2 + \text{CH}_3\text{OCH}_3 \rightarrow \text{CH}_3 + \text{CH}_2\text{OCH}_3
\]

\[
\text{CH}_2\text{OCH}_3 + R \rightarrow \text{CH}_3\text{CHO} + \text{RH}
\]

as a deep seated rearrangement of atoms would be required. Abstraction of H from MeOMe has of course been observed with methyl radicals\(^{37}\) and at high temperature (270-400) where CH₂O is formed by the decomposition of CH₂OCH₃. The reactions which take place are probably:

\[
\text{CH}_3 + \text{CH}_3\text{OCH}_3 \rightarrow \text{CH}_4 + \text{CH}_2\text{OCH}_3 \quad (5)
\]

\[
\text{CH}_2\text{OCH}_3 \rightarrow \text{HCHO} \quad (6)
\]

\[
\text{CH}_2\text{OCH}_3 + \text{CH}_3 \rightarrow \text{CH}_3\text{OC}_2\text{H}_5 \quad (7)
\]

\[
\text{CH}_2\text{OCH}_3 + \text{CH}_2\text{OCH}_3 \rightarrow X \quad (8)
\]

Reaction (5) has been studied by various workers\(^{88-91}\). Its activation energy has been shown to be 10 kcal.
3.1. METHYLENE REACTIONS WITH DIETHYL ETHER

The reactions of CH₂ with EtOEt were the first to be studied. A check on the reaction kinetics was made by the experiments where methylene was made to react with n-pentane.

Keten and n-pentane in the ratio 1:5 were irradiated to 10% decomposition. Analyses of the products were carried out on a chromatography column of F(DMP) (Table 1, 5). The products of the reaction largely from insertion

\[
\begin{align*}
&\text{H} \quad \text{H} \quad \text{H} \\
&\text{H} \quad \text{C} \quad \text{C} \quad \text{C} \quad \text{C} \quad \text{C} \quad \text{H} \\
&\text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H}
\end{align*}
\]

were 2,2-dimethyl butane, 3-methyl butane and n-hexane.

With diethyl ether in place of n-pentane, the products of insertion were expected to be EtOPr₁ and EtOPr₂. These were found but in addition two new products (A and B) appeared

\[
\begin{align*}
&\text{H} \quad \text{H} \quad \text{H} \\
&\text{H} \quad \text{C} \quad \text{C} \quad \text{O} \quad \text{C} \quad \text{C} \quad \text{H} \\
&\text{H} \quad \text{H} \quad \text{H}
\end{align*}
\]

The chromatographic conditions were varied to further test the purity of A and B. Analyses on Celite (DNP) column (Runs 24-54) showed A and B appeared before EtOEt as a single peak. On F(DMP) column the position of A was not changed but B now appeared after EtOEt, its amount relative to the propyl ethers being very small for Runs done at room temperature but somewhat larger
at 100°C. Peak B was much increased relatively when air was added to the reaction mixture.

Peak B formed with and without the addition of air appeared to be a single substance. This was shown by using different columns (C(DMP), F(DMP)) upon which the retention volume of Peak 'B' changed while that of 'A' relative to other ethers did not. Peak 'B' was finally identified as acetaldehyde which gave identical retention times on the two columns. Also the relative yield of 'A' did not change from experiments at 20°C to 100°C. Addition of propane to the system did not alter this value significantly or the relative rate of ETOPr₁. Peak 'A' was identical in shape to the higher ethers and was finally identified as MeOEt. The formation of analogous products from other ethers led to the conclusion that two additional modes of reaction of methylene with ethers were possible:

1. Abstraction Reaction, giving rise with EtOEt to acetaldehyde.

2. Displacement Reaction, giving MeOEt + ethylene.

The various modes of reaction of methylene with EtOEt will be discussed in turn.

3.2. INSERTION REACTION

As shown in the sketch in Chapter 3.1, insertion reaction leads to

\[ \text{CH}_2^+ + \text{C}_2\text{H}_5\text{OC}_2\text{H}_5 \rightarrow \text{C}_2\text{H}_5\text{O}^\text{2} \text{H} 7 \]

\[ \text{CH}_2 + \text{C}_2\text{H}_5\text{OC}_2\text{H}_5 \rightarrow \text{C}_2\text{H}_5\text{OH}(\text{CH}_3)_2 \]

The relative rate of formation of ETOPr₁/EtOPrᵡ at room temperature is given in Table 3.1.2. The average molar ratio is 1.36. Under more carefully controlled conditions, when the role of oxygen had become more clearly understood, the average value obtained was 1.75 (Table 3.1.1., Runs 416, 426) for Runs at 20°C. It is clear from the same table that the effect of
oxygen in the system is to lower the values. A value of 1.75 represents the relative rate of attack of CH_2 on four 2 C-H bonds compared to six 1 C-H bonds, i.e. the secondary bond is \( \frac{3}{2} \times 1.75 = 2.6 \) times as reactive as the primary bond.

The role of oxygen in affecting the insertion mechanism was studied by the addition of air into the reaction vessel. Fig. 8 shows that at room temperature a lowering in the values of \( \frac{R_{iso}}{R_{1n}} \) that takes place at air pressure up to 1 cm, after which there is no change - the value remaining steady at about 1.4. At 100°C the addition of O_2 has no significant effect on this ratio. The absolute amounts of both the ethers formed at room temperature are given in full in Table 3.1.1. The variation of EtOPr^1 and EtOPr^2 with respect to pressure of air was obtained by fixing the concentration and time parameter of the reaction. Fig. 4 shows the abrupt fall in the absolute EtOPr^1 produced when small amount of air was added. From the initial value of 2.2, the value at an air pressure of 10 cm comes to 0.45 or less. Similarly, the absolute amount of EtOPr^2 under similar conditions showed a decrease on the addition of air (Fig.4A). The effect is similar in both cases except that in the lower regions of air pressure the EtOPr^1 yield is affected to a greater degree as evidenced from the fall in the relative EtOPr^1 curve shown in Fig.8.

The effect of temperature on the relative yield of EtOPr^1 was determined, as shown in Table 3.1.2. The average of the molar ratio at 100°C is 1.86 compared to 1.75 at room temperature. These reactions have small difference in the activation energy.

The addition of propane to the reaction mixture was studied, the values obtained are given in Table 3.2.4. From 2-12 cms propane was added. The resultant products were analysed on F(DMP)52-72 column and the products
of reaction of CH$_2$ with EtOEt were separated from the butanes formed from the attack of iCH$_2$ on propane. A molar value of 1.82 was obtained for EtOPr$^i$/EtOPr$^n$ (Table 3.2.4). Thus we see no alteration in the mode of insertion of methylene in the presence of excess of propane. There is, on the other hand, at 100°C a distinct fall in the value $R$(EtOPr$^i$/EtOPr$^n$) in the presence of added carbon dioxide, (Table 3.2.4), where the molar ratio was 1.54. It was found, however, that an addition of small amounts of oxygen (air 1 cm or so) to the same system results in an increase in the relative yield to 1.90 in contrast to the effect without CO$_2$.

**TABLE 3.2.4.**

**Effect of added gases**

Reaction: iCH$_2$ + EtOEt at 20°C

Column: F(DMP)$_D$ (52-72)

Nitrogen flow = 17 ccs/minute

Column Temp: 20°C

<table>
<thead>
<tr>
<th>Pressure cm.</th>
<th>Normalized to EtOPr$^n$ (peak areas)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Run No.</td>
<td>Keten</td>
</tr>
<tr>
<td>---------------</td>
<td>-------</td>
</tr>
<tr>
<td>65</td>
<td>2.0</td>
</tr>
<tr>
<td>59</td>
<td>1.0</td>
</tr>
<tr>
<td>60</td>
<td>2.0</td>
</tr>
<tr>
<td>61</td>
<td>2.0</td>
</tr>
<tr>
<td>62</td>
<td>2.0</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Molar ratio:</td>
</tr>
</tbody>
</table>

At 100°C

Column: Celite (DNP) + F(DMP) 3 ft.

<table>
<thead>
<tr>
<th>CO$_2$</th>
<th>Air</th>
<th>372</th>
<th>2.6</th>
<th>8.1</th>
<th>7.2</th>
<th>0.15</th>
<th>-</th>
<th>1.17</th>
</tr>
</thead>
<tbody>
<tr>
<td>380</td>
<td>2.0</td>
<td>10.1</td>
<td>17.9</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.18</td>
<td></td>
</tr>
<tr>
<td>381</td>
<td>2.0</td>
<td>10.0</td>
<td>2.35</td>
<td>1.2</td>
<td>-</td>
<td>0.85</td>
<td>1.59</td>
<td></td>
</tr>
<tr>
<td>382</td>
<td>1.9</td>
<td>10.0</td>
<td>11.8</td>
<td>1.0</td>
<td>-</td>
<td>1.61</td>
<td>1.90</td>
<td></td>
</tr>
</tbody>
</table>

Average: 1.18

Molar: 1.54

0.76

0.85

Average: 1.61

Molar: 1.90
3.3. DISPLACEMENT REACTION

As stated earlier, the production of methyl ethyl ether from the reaction of methylene with diethyl ether was discovered during the present research. It may, for the present, be written

\[ \text{CH}_2 + \text{C}_2\text{H}_5\text{OC}_2\text{H}_5 \rightarrow \text{CH}_3\text{OC}_2\text{H}_5 + \text{C}_2\text{H}_4 \]

The position of methyl ethyl ether on different columns did not alter nor did its relative yield in the presence of propane in different concentrations. An average value 0.45 for the molar ratio MeOEt/EtOPr\textsubscript{n} was obtained in the absence of added gases which shows that the reaction is quite fast even at 20°C compared to the insertion reaction (Runs 416, 426 Table 3.1.1). Such a product could have resulted from the reaction

\[ \text{CH}_2 + \text{C}_2\text{H}_5\text{OH} \rightarrow \text{C}_2\text{H}_5\text{OCH}_3 \]

and it was for this reason that the ethers employed in these investigations were ascertained to be free of alcohol. For the sake of argument, if the displacement reaction be imagined to be an insertion into Et-O bond which is followed by H-shift from the $^2$ C-H, then we could compare its rate with that of direct insertion into $^2$ C-H bond by which EtOPr\textsubscript{i} is formed. We obtain a value of 0.45 for the rate of this reaction compared to the insertion into the primary C-H bond.

In view of the observations made under Insertion reactions, it was considered of interest to explore the effect of oxygen on the relative efficiency of attack of methylene giving displacement reaction. At room temperature, the molar ratio MeOEt/EtOPr\textsubscript{n} in the absence of added air may be taken as 0.45 (Runs 426, 451) from Table 3.1.1. Up to 45.2 cm Hg of air was added and the values obtained are given in the same table in the molar ratios. A plot of these is shown in Fig. 7 where a clear trend of
the increase is shown. At 100°C, the molar ratio was found to be 0.53 on an average (Table 3.1.2) but on the addition of air between the range 26 to 32 cms, it was found that the values are definitely increased though the scatter was large.

3.4. ABSTRACTION REACTIONS

This reaction, like the Displacement reaction, had never been reported before in ethers until a new product, acetaldehyde, was found in the present investigations. Its confirmation came from comparisons of the retention time of pure acetaldehyde on various columns. Acetaldehyde arises from hydrogen-abstraction of ether and the following scheme may be put forth at this stage.

\[
\begin{align*}
\cdot \text{CH}_2 + \text{C}_2\text{H}_5\text{OOC}_2\text{H}_5 & \rightarrow \cdot \text{CH}_3 + \text{C}_3\text{H}_5\text{OOC}_2\text{H}_5 \quad (1) \\
\cdot \text{CH}_3 + \text{C}_2\text{H}_5\text{OOC}_2\text{H}_5 & \rightarrow \text{CH}_4 + \text{C}_3\text{H}_5\text{OOC}_2\text{H}_5 \quad (2) \\
\cdot \text{C}_2\text{H}_5 + \text{C}_2\text{H}_5\text{OOC}_2\text{H}_5 & \rightarrow \text{C}_2\text{H}_6 + \text{C}_3\text{H}_5\text{OOC}_2\text{H}_5 \quad (3) \\
\text{CH}_3\text{HOC}_2\text{H}_5 & \rightarrow \text{CH}_3\text{CHO} + \cdot \text{C}_2\text{H}_5 \quad (4) \\
2 \cdot \text{C}_2\text{H}_5 & \rightarrow \text{C}_4\text{H}_{10} \quad (5) \\
2 \cdot \text{CH}_3 & \rightarrow \text{C}_2\text{H}_6 \quad (6)
\end{align*}
\]

This shows a monoradical behaviour of methylene. For experiments done at room temperature the results are given in Table 3.1.1. where (Runs 426, 451) in the absence of oxygen (air) the molar ratio \( \text{CH}_3\text{CHO}/\text{EtCPr}^n \) = 0.21. At 100°C, this value increased ten-fold (Run 466, Table 3.1.2) where it was further found that separation of \( \text{CH}_3\text{CHO} \) on Celite (DNP) column was poor and hence the figures for acetaldehyde vary considerably.

In the presence of oxygen the formation of acetaldehyde is greatly increased. This may be explained by supposing that the ethyl
radicals undergo, besides 2, 3, 5, 6, and cross combinations, the following reactions:

\[
\begin{align*}
C_2H_5 + O_2 & \rightarrow C_2H_5O_2 \\
C_2H_5O_2 & \rightarrow CH_2CHO + OH \\
CH + RH & \rightarrow R + H_2O \\
2 C_2H_5O_2 & \rightarrow CH_3CHO + H_2O
\end{align*}
\]

This closely follows Noyes and Finkelstein\(^{106}\)'s mechanism for the disappearance of .C\(_2\)H\(_5\) formed from EtCOEt. The indication for the presence of water as a minor constituent in the products was a negative peak in a chromatogram. Methyl radicals may react as follows:

\[
\begin{align*}
.CH_3 + O_2 & \rightarrow CH_3O_2 \\
CH_3O_2 + CH_3 & \rightarrow CH_3OH + CH_2O \\
mCH_2O + hy & \rightarrow (CH_2O)_n
\end{align*}
\]

3.5. **ADDITIONAL PRODUCTS FORMED IN PRESENCE OF OXYGEN**

During the course of studies on the role of oxygen, product analyses led to an unexpected trend in the increase of R(EtOPr\(^{1}/\)EtOPr\(^{n}\)). Change of the chromatographic column soon revealed that the EtOPr\(^{n}\) peak masked a new product. In a large number of trial runs (not included) separation of the new product or products was incompletely achieved. Under one set of conditions, for example, column F(DMP)D gave EtOPr\(^{1}\) peak overlapped with the unknown, while Celite (DNP) column showed that the unknown appear along with EtOPr\(^{n}\) on the chromatograms. The apparent ratio of EtOPr\(^{1}/\)EtOPr\(^{n}\) consequently decreased owing to the impurity appearing under EtOPr\(^{n}\) peak and was found to be 0.71 instead of 1.6 (Runs 311-313). Product analyses on different columns were done to separate out the unknown product.
from the EtOPr\textsuperscript{n}. Steps were taken to ensure that none of the known product was contaminated by an unknown one. Columns of Celite (80-100) carrying 20% squalane or nitrobenzene or polyethylene glycol were employed for the purpose individually, as well as in combination, to obtain an ideal polarity in the liquid phase. As a result of a number of trials, a combination of Celite (DNP)\textsuperscript{1/2} + Celite (Squalane) was found to give a neat separation of all the known products plus one "unknown" called "X".

On column C(80-100) squalane, the other unknown product "Y" - later identified to be ethyl formate - was separable (Run 407) and quantitatively found to be twice the product "X" - later identified to be ethyl acetate - the disadvantage on this column, however, being that the product "X" referred to above was mixed with EtOPr\textsuperscript{n}. Only by carrying out a separate analysis did it seem possible to estimate correctly the two products quantitatively. On the combined column C(Squalane) + C(DNP)\textsuperscript{1/2}, product "Y" (ethyl formate) eluted along with the substrate diethyl ether and was not followed in detail, and attention was focussed on ethyl acetate expecting that the other ester would behave in a similar manner.

3.5.1. IDENTIFICATION OF PRODUCTS X AND Y

Since these products were being produced only in the presence of oxygen, search was made for peroxides of the form EtOOPr. Adequate quantities were collected using a large reaction vessel (250 mls). Each product was a viscous fluid. Since X appeared soon after EtOPr\textsuperscript{n} and the boiling point of peroxide was close to it i.e.

\[
\begin{align*}
\text{EtOPr}^n & \quad \text{B.P.} = 64\,^\circ\text{C} \\
\text{C}_2\text{H}_5\text{OOPr} & \quad \text{B.P.} = 65\,^\circ\text{C}
\end{align*}
\]

tests for peroxides were performed. Reduction of a peroxide by Zn, Hg (amalgam)
should have given alcohols. Thus

\[ \text{C}_2\text{H}_5\text{OOC}_3\text{H}_7 + \text{H} \rightarrow \text{C}_2\text{H}_5\text{OH} + \text{C}_3\text{H}_7\text{OH} \]

However, no evidence for alcohols was found chromatographically.

There was also the possibility of the unknowns being acids resulting from oxidation of aldehydes formed from ethers, but none were found. Even the formation of cyclized product like dioxane were looked for with negative result. Nonetheless these experiments established clearly that the products, large as they were, result from some direct reaction and were not by-products.

The other reasoning was based on the following relationship between data on the amount of product "X" and "X+EtOPr^m" given in the table below:

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Air P.cm.</th>
<th>&quot;X&quot;</th>
<th>EtOPr^m</th>
<th>X/X+EtOPr^m</th>
</tr>
</thead>
<tbody>
<tr>
<td>375</td>
<td>5.8</td>
<td>44.7</td>
<td>31.48</td>
<td>0.59</td>
</tr>
<tr>
<td>376</td>
<td>12.8</td>
<td>115.9</td>
<td>51.2</td>
<td>0.69</td>
</tr>
<tr>
<td>377</td>
<td>23.8</td>
<td>52.5</td>
<td>32.0</td>
<td>0.62</td>
</tr>
<tr>
<td>378</td>
<td>15.7</td>
<td>95.3</td>
<td>41.8</td>
<td>0.69</td>
</tr>
<tr>
<td>343</td>
<td>28.4</td>
<td>80.5</td>
<td>46.9</td>
<td>0.63</td>
</tr>
<tr>
<td>348</td>
<td>14.7</td>
<td>35.0</td>
<td>20.4</td>
<td>0.63</td>
</tr>
<tr>
<td>Average</td>
<td></td>
<td></td>
<td></td>
<td>0.64</td>
</tr>
</tbody>
</table>

Assuming the sensitivity of the product "X" and EtOPr^m were same it seemed, from the constancy of the ratios, that an activated complex when formed breaks up into these products. The ratio 2/3 (approx.) for X/(X + EtOPr^m) showed X is twice EtOPr^m within wide limits of added air. Infra-red
examination of the preliminary product showed it has a carbonyl group but no comparison with an aldehyde, ketone, or acid was available.

In order to decide whether the product results from an attack of CH₂ or CH₃ (and oxygen), experiments were carried out using acetone as source for methyl radicals. It was found that in the absence of air (oxygen), CH₃ + EtOEt did not give rise to "X" and "Y" but when air was present these products were formed (Runs 407-411). Adequate quantities of the oxygenated product "X" were prepared using a reaction vessel of 250 mls capacity and a combination of Celite (DNP) and Celite (squalane) columns. About 100 micromoles of this viscous liquid were collected and repurified on two more columns. These columns were F(DMP 52-72) and G(DNP 80-100) treated with 20% of liquid phase using excess of CCl₄, the latter having been completely removed. This was done to ensure against interference (by solvents like acetone) in the infra-red spectra. The product "X" after two successive purifications was passed through the Celite (Squalane) column on which the product "Y" was found to separate from it completely.

The infra-red spectrum of "Y" gave sharp intensities at 1750, 1350, 1250, and 1100 cm⁻¹ and was suggestive of esters. Of all the possible esters, ethyl acetate was found to fit in with the spectra as well as with the chromatographic evidence. The latter evidence was obtained by first mixing about 5 μ-moles of methyl acetate, ethyl formate and ethyl acetate in separate tests. Only the ethyl acetate appeared as a single peak with "X" on chromatogram, even when different columns were used.

A procedure similar to that described above was followed in the separation of product "Y" and its identification. The product was first chromatographed on celite (squalane) column, where EtOPri does not interfere,
followed by successive chromatography on C(DNP) and F(DMP) columns. The identification of "Y" as ethyl formate was established chromatographically as well as spectroscopically. Its spectrum was identical to that obtained with pure ethyl formate.

3.5.1. CHANGE IN YIELDS OF OXYGENATED PRODUCTS WITH OXYGEN PRESSURE

The absolute amounts of ethyl acetate and ethyl formate increased with the increase in oxygen pressure in the system. Ethyl acetate formation was studied in detail (Fig.3) and its rate of formation seemed to vary in a manner similar to that of acetaldehyde (Fig.10). Both show a sharp rise in the initial region of air pressure increase; acetaldehyde rises about five-fold or more with an air pressure 2.5 cm Hg. From an air pressure of about 3 cm Hg onwards it shows a fall but becomes steady from 10 cm pressure onwards and is still more than thrice its original value. The relative amount of acetaldehyde (CH$_3$CHO/EtOPr$^+$) (Fig.6) shows an increase with the increase in air pressure up to about 20 cm, after which it tends to remain steady where the side reactions assume more importance. It is here that the formation of esters is increasing, as evidenced from the relative amount of ethyl acetate produced (Fig.5) and the excess oxygen may be reacting with the ether radicals formed by steps (1), (2), (3), before they have a chance to decompose as in step (4) (Section 3.4). At 100$^\circ$C, the relative yield of acetaldehyde increases from 0.4 to about 13.0 on the addition of oxygen to the system (Table 3.1.2, compare Runs 71 and 462). This 45-fold increase in the relative yield further strongly suggests the occurrence of a chain reaction. Similarly, experiments done at room temperature show an increase in the relative yield of acetaldehyde on the addition of oxygen (Fig.6). At 25 cm Hg air pressure an 11-fold increase occurs.
The results may be qualitatively explained on the basis of the following reactions:

\[ ^\text{CH}_2 + \text{EtOEt} \rightarrow \text{CH}_3\text{CHOC}_2\text{H}_5 + ^\text{CH}_3 \]  

\[ \text{X} + \text{EtOEt} \rightarrow \text{CH}_3\text{CHOC}_2\text{H}_5 + \text{XH} \]  

\[(X, \text{any monoradical as } \text{CH}_3, \text{C}_2\text{H}_5, \text{OH}, \text{CH}_3\text{O})..(2)\]

\[ \text{CH}_3\text{CHOC}_2\text{H}_5 + \text{O}_2 \rightarrow \text{CH}_3\text{COOC}_2\text{H}_5 + .\text{OH} \]  

\[ .\text{H} \rightarrow \text{HCOOC}_2\text{H}_5 + .\text{OCH}_3 \]  

\[ \text{CH}_3\text{CHOC}_2\text{H}_5 \rightarrow \text{CH}_3\text{CHO} + .\text{C}_2\text{H}_5 \]  

\[ .\text{C}_2\text{H}_5 + \text{O}_2 \rightarrow .\text{CH}_3\text{CHO} + .\text{OH} \]  

This is confirmed by the fact that all the three oxygenated products are formed from experiments with CH\(_3\) + O\(_2\) + EtOEt.

The absolute relative yields of esters are given in Table 3.1.1. A plot of the absolute yields at 20°C (Fig. 3) shows a rise up to a pressure of 5 cm of air followed by a gradual decrease up to 10 cm of air; thereafter the yield is constant. Since the time of irradiation was the same in all these runs it was possible that the initial rise resulted from complete consumption of the oxygen before the end of the irradiation. The fall of both 5 and 10 cm air must however result from secondary reactions.

In order to establish this point more firmly, experiments were done with fixed composition of keten and ether and air. An air pressure of 2 cm was chosen from the rising region of the curve (Fig. 3). On changing the time of irradiation the areas of ester obtained were:

<table>
<thead>
<tr>
<th>Time of Irradiation</th>
<th>Peak Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>15 minutes</td>
<td>9.1</td>
</tr>
<tr>
<td>30 &quot;</td>
<td>10.0</td>
</tr>
<tr>
<td>60 &quot;</td>
<td>9.3</td>
</tr>
</tbody>
</table>

There was no increase in the yield of ethyl acetate which established that the ester in the rising region is coming from a complete consumption of oxygen.
added. The shape of the curve (Fig. 5) represents the relative yield of ethyl acetate with respect to air. The first sharp rise is followed by another rising region after a pressure of 20 cm of air.

The yield of ethyl formate was about twice that of ethyl acetate and was by far the largest product of the reaction (Run 407). Thus step (4) is faster than step (3) shown above. Ethyl formate formed by step (4) above (3.5.1.1.) involves the breakage of C-CH₃ bond which, being weaker than C-H bond involved in step (3), is possibly one of the reasons for the larger yields of ethyl formate compared to that of ethyl acetate.

At 100°C

\[
\begin{align*}
1.0 & \quad \rightarrow \\
H & \quad \overset{2.79}{\searrow} \quad 1.14 \\
H & \quad \overset{2.6}{\searrow} \\
\end{align*}
\]

At 20°C

\[
\begin{align*}
1.0 & \quad \rightarrow \\
H & \quad \overset{2.6}{\searrow}
\end{align*}
\]
### TABLE 3.1.1.

**Reaction:** CH₂ + EtOEt at Room Temp. (Ketone:EtOEt: 1:2)

**Duration of Run:** 30 mts.

**Column:** Celite (80-100) DNP ½ + C(80-100) Squalane(S)

**N₂ Flow:** 21-22 C.C./mt.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Air</th>
<th>Column</th>
<th>CH₃OH</th>
<th>MeOEt</th>
<th>EtOPr¹</th>
<th>EtOPr²</th>
<th>Et.Acet.</th>
<th>Et. Form.</th>
<th>Normalised to EtOPr²</th>
</tr>
</thead>
<tbody>
<tr>
<td>406</td>
<td>Nil</td>
<td>C(Sq)S</td>
<td>0.48</td>
<td>0.24</td>
<td>0.46</td>
<td>0.24</td>
<td>-</td>
<td>-</td>
<td>0.36</td>
</tr>
<tr>
<td>416</td>
<td>&quot;</td>
<td></td>
<td>0.256</td>
<td>0.22</td>
<td>0.21</td>
<td>0.21</td>
<td>-</td>
<td>-</td>
<td>0.22</td>
</tr>
<tr>
<td>426</td>
<td>&quot;</td>
<td></td>
<td>0.16</td>
<td>0.36</td>
<td>0.32</td>
<td>0.74</td>
<td>-</td>
<td>-</td>
<td>0.20</td>
</tr>
<tr>
<td>451</td>
<td>&quot;</td>
<td></td>
<td>0.26</td>
<td>0.54</td>
<td>2.25</td>
<td>1.40</td>
<td>-</td>
<td>-</td>
<td>0.01</td>
</tr>
<tr>
<td>(224)</td>
<td>&quot;</td>
<td></td>
<td>0.09</td>
<td>0.09</td>
<td>0.97</td>
<td>0.62</td>
<td>-</td>
<td>-</td>
<td>0.15</td>
</tr>
<tr>
<td>433</td>
<td>0.3</td>
<td></td>
<td>0.29</td>
<td>0.33</td>
<td>1.14</td>
<td>0.72</td>
<td>0.12</td>
<td>-</td>
<td>0.45</td>
</tr>
<tr>
<td>432</td>
<td>0.7</td>
<td></td>
<td>0.438</td>
<td>0.36</td>
<td>0.91</td>
<td>0.68</td>
<td>1.12</td>
<td>-</td>
<td>0.47</td>
</tr>
<tr>
<td>430</td>
<td>1.7</td>
<td></td>
<td>0.79</td>
<td>0.37</td>
<td>0.86</td>
<td>0.63</td>
<td>1.29</td>
<td>-</td>
<td>0.53</td>
</tr>
<tr>
<td>438</td>
<td>2.25</td>
<td></td>
<td>1.13</td>
<td>0.57</td>
<td>1.45</td>
<td>0.98</td>
<td>1.81</td>
<td>-</td>
<td>1.34</td>
</tr>
<tr>
<td>434</td>
<td>5.0</td>
<td></td>
<td>0.75</td>
<td>0.30</td>
<td>0.94</td>
<td>0.68</td>
<td>1.49</td>
<td>-</td>
<td>1.50</td>
</tr>
<tr>
<td>439</td>
<td>6.6</td>
<td></td>
<td>0.73</td>
<td>0.31</td>
<td>1.02</td>
<td>0.68</td>
<td>1.57</td>
<td>-</td>
<td>1.65</td>
</tr>
<tr>
<td>436</td>
<td>8.5</td>
<td></td>
<td>0.86</td>
<td>0.35</td>
<td>0.72</td>
<td>0.48</td>
<td>1.1</td>
<td>-</td>
<td>1.79</td>
</tr>
<tr>
<td>416</td>
<td>8.7</td>
<td></td>
<td>0.90</td>
<td>(0.29)</td>
<td>(1.97)</td>
<td>0.56</td>
<td>0.62</td>
<td>-</td>
<td>1.61</td>
</tr>
<tr>
<td>421</td>
<td>8.9</td>
<td></td>
<td>0.12</td>
<td>0.08</td>
<td>0.42</td>
<td>0.31</td>
<td>0.62</td>
<td>-</td>
<td>1.35</td>
</tr>
<tr>
<td>407</td>
<td>9.1</td>
<td></td>
<td>0.62</td>
<td>0.18</td>
<td>0.51</td>
<td>0.35</td>
<td>0.78</td>
<td>-</td>
<td>1.35</td>
</tr>
<tr>
<td>508</td>
<td>10.5</td>
<td></td>
<td>0.78</td>
<td>0.34</td>
<td>0.59</td>
<td>0.45</td>
<td>0.977</td>
<td>-</td>
<td>2.23</td>
</tr>
<tr>
<td>420</td>
<td>10.9</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.44</td>
</tr>
<tr>
<td>449</td>
<td>13.3</td>
<td></td>
<td>0.87</td>
<td>0.47</td>
<td>0.78</td>
<td>0.535</td>
<td>1.165</td>
<td>-</td>
<td>1.48</td>
</tr>
<tr>
<td>446</td>
<td>14.7</td>
<td></td>
<td>0.74</td>
<td>0.35</td>
<td>0.60</td>
<td>0.45</td>
<td>1.04</td>
<td>-</td>
<td>1.33</td>
</tr>
<tr>
<td>429</td>
<td>15.1</td>
<td></td>
<td>0.62</td>
<td>0.25</td>
<td>0.27</td>
<td>0.20</td>
<td>0.51</td>
<td>-</td>
<td>1.35</td>
</tr>
<tr>
<td>(425)</td>
<td>15.5</td>
<td></td>
<td>0.34</td>
<td>0.30</td>
<td>1.17</td>
<td>0.84</td>
<td>-</td>
<td>-</td>
<td>1.39</td>
</tr>
<tr>
<td>442</td>
<td>20.2</td>
<td></td>
<td>0.41</td>
<td>0.17</td>
<td>0.195</td>
<td>0.13</td>
<td>0.226</td>
<td>-</td>
<td>1.31</td>
</tr>
<tr>
<td>(437)</td>
<td>20.5</td>
<td></td>
<td>0.70</td>
<td>0.33</td>
<td>0.44</td>
<td>0.318</td>
<td>0.92</td>
<td>-</td>
<td>1.30</td>
</tr>
<tr>
<td>435</td>
<td>20.8</td>
<td></td>
<td>0.49</td>
<td>0.18</td>
<td>0.26</td>
<td>0.19</td>
<td>0.45</td>
<td>-</td>
<td>1.37</td>
</tr>
<tr>
<td>444</td>
<td>24.7</td>
<td></td>
<td>0.61</td>
<td>0.34</td>
<td>0.36</td>
<td>0.28</td>
<td>0.80</td>
<td>-</td>
<td>1.32</td>
</tr>
<tr>
<td>436</td>
<td>27.9</td>
<td></td>
<td>0.63</td>
<td>0.22</td>
<td>0.26</td>
<td>0.20</td>
<td>0.76</td>
<td>-</td>
<td>1.30</td>
</tr>
<tr>
<td>431</td>
<td>28.1</td>
<td></td>
<td>0.62</td>
<td>0.28</td>
<td>0.34</td>
<td>0.26</td>
<td>0.83</td>
<td>-</td>
<td>1.30</td>
</tr>
<tr>
<td>442</td>
<td>29.4</td>
<td></td>
<td>0.74</td>
<td>0.32</td>
<td>0.46</td>
<td>0.33</td>
<td>0.87</td>
<td>-</td>
<td>1.39</td>
</tr>
<tr>
<td>455</td>
<td>34.8</td>
<td></td>
<td>0.67</td>
<td>0.36</td>
<td>0.42</td>
<td>0.30</td>
<td>0.88</td>
<td>-</td>
<td>1.40</td>
</tr>
<tr>
<td>438</td>
<td>35.5</td>
<td></td>
<td>0.71</td>
<td>0.36</td>
<td>0.45</td>
<td>0.32</td>
<td>1.11</td>
<td>-</td>
<td>1.41</td>
</tr>
<tr>
<td>453</td>
<td>39.1</td>
<td></td>
<td>0.73</td>
<td>0.38</td>
<td>0.42</td>
<td>0.32</td>
<td>1.07</td>
<td>-</td>
<td>1.31</td>
</tr>
<tr>
<td>(456)</td>
<td>39.5</td>
<td></td>
<td>0.29</td>
<td>0.15</td>
<td>0.10</td>
<td>0.30</td>
<td>0.88</td>
<td>-</td>
<td>1.34</td>
</tr>
<tr>
<td>(460)</td>
<td>44.1</td>
<td></td>
<td>0.30</td>
<td>0.21</td>
<td>0.15</td>
<td>0.11</td>
<td>0.49</td>
<td>-</td>
<td>1.36</td>
</tr>
<tr>
<td>452</td>
<td>45.2</td>
<td></td>
<td>0.69</td>
<td>0.36</td>
<td>0.31</td>
<td>0.23</td>
<td>0.86</td>
<td>-</td>
<td>1.35</td>
</tr>
</tbody>
</table>
**TABLE 3.1.2.**

Reaction: \( \text{CH}_2 + \text{EtOEt} \) at 100°C

Column Temp: 20°C

\( \text{N}_2 \) Flow: 17-19 ml/s

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Chromat.</th>
<th>Keten</th>
<th>Ether</th>
<th>Duration</th>
<th>Normalised to MeOEt</th>
<th>CH_2CHO</th>
<th>EtOPr_n</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Column P.Cm.</td>
<td>P.Cm.</td>
<td>P.Cm.</td>
<td>Hr.mts.</td>
<td>P.Cm.</td>
<td>P.Cm.</td>
<td>P.Cm.</td>
</tr>
<tr>
<td>71</td>
<td>F(DMP)D 1.0</td>
<td>2.0</td>
<td>0-45</td>
<td>Nil</td>
<td>0.21</td>
<td>0.40</td>
<td>1.58</td>
</tr>
<tr>
<td>72</td>
<td>&quot; 2.0</td>
<td>6.0</td>
<td>0-45</td>
<td>&quot;</td>
<td>0.18</td>
<td>0.35</td>
<td>1.51</td>
</tr>
<tr>
<td>73</td>
<td>&quot; 2.0</td>
<td>10.0</td>
<td>1-00</td>
<td>&quot;</td>
<td>0.19</td>
<td>0.37</td>
<td>1.54</td>
</tr>
<tr>
<td>75</td>
<td>&quot; 5.0</td>
<td>12.0</td>
<td>1-30</td>
<td>&quot;</td>
<td>0.18</td>
<td>0.35</td>
<td>1.56</td>
</tr>
<tr>
<td>76</td>
<td>&quot; 4.0</td>
<td>13.8</td>
<td>1-30</td>
<td>&quot;</td>
<td>0.18</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>74</td>
<td>&quot; 3.0</td>
<td>12.0</td>
<td>2-00</td>
<td>&quot;</td>
<td>0.18</td>
<td>0.35</td>
<td>1.55</td>
</tr>
<tr>
<td>316</td>
<td>&quot; 2.1</td>
<td>12.1</td>
<td>1-00</td>
<td>&quot;</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>318</td>
<td>&quot; 2.0</td>
<td>12.1</td>
<td>2-00</td>
<td>(</td>
<td>0.55</td>
<td>1.40</td>
<td></td>
</tr>
<tr>
<td>342</td>
<td>Cel(DNP) 2.0</td>
<td>12.0</td>
<td>2-00</td>
<td>&quot;</td>
<td>0.66</td>
<td>1.52</td>
<td></td>
</tr>
<tr>
<td>345</td>
<td>&quot; 2.0</td>
<td>&quot;</td>
<td>2-00</td>
<td>&quot;</td>
<td>-</td>
<td>-</td>
<td>1.61</td>
</tr>
<tr>
<td>352</td>
<td>(Cel + F(DMP)) 11.9</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>0.62</td>
<td>1.59</td>
<td></td>
</tr>
<tr>
<td>354</td>
<td>F(DMP)D 2.0</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>0.22</td>
<td>0.66</td>
<td>1.48</td>
</tr>
<tr>
<td>355</td>
<td>Celite &quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>0.22</td>
<td>-</td>
<td>1.57</td>
</tr>
<tr>
<td>357</td>
<td>&quot; 11.9</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>0.16</td>
<td>-</td>
<td>1.51</td>
</tr>
<tr>
<td>358</td>
<td>&quot; 11.8</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>0.23</td>
<td>-</td>
<td>1.62</td>
</tr>
<tr>
<td>350</td>
<td>(G(DNP) + F(DMP)) 11.9</td>
<td>&quot;</td>
<td>&quot;</td>
<td>3-48</td>
<td>0.55</td>
<td>1.57</td>
<td></td>
</tr>
<tr>
<td>352</td>
<td>(F(DMP)) &quot;</td>
<td>&quot;</td>
<td>2-00</td>
<td>&quot;</td>
<td>0.51</td>
<td>1.49</td>
<td></td>
</tr>
</tbody>
</table>

**Average:**

- Molar ratio: 0.38

**Effect of Oxygen:** Columns: Celite (squalane) + Cel(DNP)\( \frac{1}{3} \).

**Et Acetat**

<table>
<thead>
<tr>
<th></th>
<th>1.0</th>
<th>1.9</th>
<th>0-30</th>
<th>27.1</th>
<th>1.0</th>
<th>15.7</th>
<th>1.69</th>
<th>3.3</th>
</tr>
</thead>
<tbody>
<tr>
<td>466</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.30</td>
<td>2.0</td>
<td>1.62</td>
<td>Nil</td>
</tr>
<tr>
<td>458</td>
<td>1.0</td>
<td>1.9</td>
<td>&quot;</td>
<td>26.9</td>
<td>1.0</td>
<td>15.7</td>
<td>1.69</td>
<td>3.3</td>
</tr>
<tr>
<td>460</td>
<td>1.0</td>
<td>2.0</td>
<td>&quot;</td>
<td>27.1</td>
<td>1.0</td>
<td>15.7</td>
<td>1.69</td>
<td>3.3</td>
</tr>
<tr>
<td>458</td>
<td>1.0</td>
<td>1.9</td>
<td>&quot;</td>
<td>27.0</td>
<td>1.0</td>
<td>13.3</td>
<td>1.50</td>
<td>3.87</td>
</tr>
<tr>
<td>459</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>26.8</td>
<td>0.97</td>
<td>10.3</td>
<td>1.53</td>
<td>5.27</td>
</tr>
<tr>
<td>463</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>31.6</td>
<td>1.3</td>
<td>18.0</td>
<td>1.66</td>
<td>5.6</td>
</tr>
<tr>
<td>462</td>
<td>&quot;</td>
<td>&quot;</td>
<td>2.0</td>
<td>29.0</td>
<td>0.82</td>
<td>15.4</td>
<td>1.54</td>
<td>4.54</td>
</tr>
</tbody>
</table>

**Average:**

- Molar ratio: 1.60

**Variates:**

- with air
- pressure.
FIG 3

ABS: Et ACETATE

Moles
CHAPTER 4

4.1. REACTIONS OF CH₂ WITH ETOPr₁₁

In order to understand the effect of the asymmetry of a molecule on the relative rate of attack of CH₂, this ether was selected for study. Mixtures of ketene and ether in the ratio 1:1, 1:2, 1:3, keeping total pressure below 15 cm, were irradiated to about 20% decomposition of keten. The chromatograms showed that about ten products were formed. These arose from:

1. Insertion Reaction:

   \[
   \begin{align*}
   CH₂ + C₂H₅OC₃H₇ & \rightarrow C₃H₇OC₂H₇ & \text{(1)} \\
   & \rightarrow \text{iso } C₃H₇OC₃H₇ & \text{(2)} \\
   & \rightarrow C₃H₇OC₄H₉ & \text{(3)} \\
   & \rightarrow C₂H₅O \text{ iso } C₄H₉ & \text{(4)} \\
   & \rightarrow C₂H₅O \text{ sec } C₄H₉ & \text{(5)}
   \end{align*}
   \]

2. Displacement Reaction:

   \[
   \begin{align*}
   CH₂ + C₂H₅OC₃H₇ & \rightarrow CH₃OC₃H₇ + C₂H₄ & \text{(6)} \\
   & \rightarrow CH₃OC₂H₅ + C₂H₆ & \text{(7)}
   \end{align*}
   \]

3. Abstraction Reaction:

   \[
   \begin{align*}
   CH₂ + C₂H₅OC₃H₇ & \rightarrow CH₃ + C₃H₇ + CH₃CHO & \text{(8)} \\
   & \rightarrow CH₃ + C₂H₅ + C₂H₅CHO & \text{(9)}
   \end{align*}
   \]

where the methyl and ethyl radical may further abstract hydrogen or dimerise etc.

4.1.1. INSERTION REACTIONS

The insertion of methylene into various C–H bonds of ethyl propyl ether gave rise to the following products:
All the five ethers have been found and the relative rates of attack of bonds is shown in the figure inset. Due to the close boiling point of product 3 and 4, the insertion at c and d at 20°C could not be separated, though for 100°C the molar values c/a, d/a have been estimated to be 1.16 and 0.86 respectively. In view of small change for attack b from 20°C to 100°C, attack c and d are unlikely to be much different from the values at 100°C. Their peak areas were estimated by drawing a vertical division between them and were inevitably somewhat in error. They are reported as the combined area in the table.

It was possible, however, to separate Pr^1OFPr^m from EtOBu^s where a reasonable estimate can be derived for the attack b/a and c/a. At 100°C, the molar ratio for the former was 1.22 and the latter 1.16 (Table 4.1.1.) each for two \( \Theta \) C-H bonds compared to three \( \Theta \) ones. A correction factor \( \frac{3}{2} \) therefore gives ratios 1.83 and 1.74 respectively which shows preference of attack on \( \Theta \) 2 C-H bond. For \( \beta \) 2 C-H bond the molar ratio for the product
EtOBu was 0.86 and comes to 1.29 per bond. Thus we have a descending order of reactivity 1.74, 1.29, 0.92 with C-H bonds on \( \alpha \), \( \beta \), and \( \gamma \) carbon atom in propyl group of ether. For EtOBu, where three \( \circ \) C-H bonds of propyl group compete with the corresponding three on ethyl side of the ether molecule, a molar ratio 0.87 for 20°C and 0.92 for 100°C again indicates a small preference of attack on the ethyl side. If one considers the preference of attack at the \( \circ \) C-H bond in MeOMe which was 1.72 compared to 1.00 in those in EtOEt to 0.92 for those on the propyl side in EtOPr, the influence of the oxygen of ether on such insertions may be substantiated. Thus closer the primary bonds are to the oxygen atom, higher is the rate of insertion reaction.

At 100°C, the molar relative rate of attack on \( \alpha \) carbon (C-H) is 1.74 based on the amount of EtOBu formed. It will be noticed that in Table 4.1.1. EtOBu and EtOBu being mixed, an indirect calculation had to be made. In some cases the EtOBu and PrOPr had to be combined for area computation since arbitrary division of overlapping peaks was not regarded as reliable. The separation of EtOBu was, however, achieved using Celite(DNP) column (I), as well as F(DMP) (20% Nitrobenzene) column. The latter (Runs 97,98) gave lower values, their average being 3.44 shown in the last but one column of Table 4.1.1., which is lower than the corresponding cumulative figure 3.8 obtained on Celite (Runs 471,473,475). The nitrobenzene column was the first to be used and it is possible that, on fresh packing, there is some loss of ethers due to irreversible absorption. For obtaining the relative rate of attack at C-H bond \( \beta \) to oxygen of ether on propyl group, the molar ratio 0.86 for EtOBu at 100°C represents an average value. This being for two C-H bonds \( \beta \) to oxygen means 1.29 per bond.
4.1.2. **DISPLACEMENT REACTION**

Methylene has been found to give a displacement reaction with EtOPr\textsuperscript{R} to yield two sets of products. By reaction (6) (section 4.1.) methyl propyl ether and ethylene are formed and from (7) methyl ethyl ether and propylene are produced. Quantitative measurements of the lower ethers produced were carried out at two temperatures only. The molar ratio MeOEt/Pr\textsuperscript{R}OPr\textsuperscript{R} at 20°C was found to be 0.20, while at 100°C, it was 0.24. Similarly the molar ratio MeOPr\textsuperscript{R}/Pr\textsuperscript{R}OPr\textsuperscript{R} at 20°C was 0.30 and rises to 0.37 at 100°C (Table 4.1.1., 4.1.2.). These reactions again seem to have low activation energies.

4.1.3. **ABSTRACTION REACTION**

It being known from the studies of diethyl ether that methylene abstracts secondary hydrogen to yield acetaldehyde, the same reaction gave acetaldehyde from attack on ethyl side of EtOPr\textsuperscript{R}. The H-abstraction from \( \text{C-H} \) bonds in propyl side yielded propionaldehyde as shown in step 9 in section 4.1. The relative rates of formation of both the aldehydes have been measured and are given in Tables 4.1.1., 4.1.2. At 100°C, the relative yields were considerably higher but were very irreproducible. Only at room temperature (Table 4.1.2.) could any reliable estimate of their relative rates of formation be obtained. At 20°C the molar ratios for acetaldehyde and propionaldehyde was found to be same viz. 0.5 for either of them. A discussion of these reactions and role of oxygen will be taken up in Section 6.4. (Chapter 6).
### Table 4.1.1.

$\text{C}_8 \text{H}_2 + \text{Et}_0 \text{Pr}_n$ at 100°C

Peak areas normalized to Di Pr$^n$ ether.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>C(DNP)</th>
<th>CH$_2$CHO</th>
<th>MeO Et</th>
<th>C$_2$H$_5$CHO</th>
<th>MeO Pr$^n$</th>
<th>n-C$_6$</th>
<th>EtO</th>
<th>EtO</th>
<th>Pr$^i$ O</th>
<th>EtO Bu$^i$</th>
<th>EtO Bu$^n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>469</td>
<td>1+4</td>
<td>1.67</td>
<td>0.28</td>
<td>1.69</td>
<td>0.41</td>
<td></td>
<td>1.43</td>
<td>(2.5)</td>
<td>0.51</td>
<td>(4.44)</td>
<td>1.04</td>
</tr>
<tr>
<td>470</td>
<td>4</td>
<td>2.44</td>
<td>0.55</td>
<td>0.83</td>
<td>0.46</td>
<td></td>
<td>Impure</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>471</td>
<td>&quot;</td>
<td>2.92</td>
<td>0.63</td>
<td>1.74</td>
<td>0.50</td>
<td>0.39</td>
<td>1.53</td>
<td>2.26</td>
<td>3.79</td>
<td>1.32</td>
<td></td>
</tr>
<tr>
<td>472</td>
<td>&quot;</td>
<td>2.70</td>
<td>1.29</td>
<td>1.61</td>
<td>0.44</td>
<td>(0.40)</td>
<td>1.77</td>
<td>3.22</td>
<td>(4.99)</td>
<td>1.34</td>
<td></td>
</tr>
<tr>
<td>473</td>
<td>&quot;</td>
<td>3.25</td>
<td>0.83</td>
<td>1.95</td>
<td>0.32</td>
<td>0.43</td>
<td>1.25</td>
<td>2.54</td>
<td>3.79</td>
<td>1.18</td>
<td></td>
</tr>
<tr>
<td>474</td>
<td>1</td>
<td>0.54</td>
<td>0.87</td>
<td>0.53</td>
<td>0.28</td>
<td>0.61</td>
<td>2.1</td>
<td>1.87+.4</td>
<td>(4.37)</td>
<td>1.37</td>
<td></td>
</tr>
<tr>
<td>475</td>
<td>4</td>
<td>0.95</td>
<td>0.197</td>
<td>0.72</td>
<td>0.25</td>
<td>0.46</td>
<td>1.30</td>
<td>2.5</td>
<td>3.80</td>
<td>1.28</td>
<td></td>
</tr>
<tr>
<td>476</td>
<td>4 Double</td>
<td>1.97</td>
<td>0.21</td>
<td>2.48</td>
<td>0.34</td>
<td>0.41</td>
<td>1.59</td>
<td>2.6</td>
<td>(4.19)</td>
<td>1.11</td>
<td></td>
</tr>
<tr>
<td>78</td>
<td>F(DNP)$^5$</td>
<td>Impure</td>
<td>2.37</td>
<td>1.45</td>
<td>(1.86)</td>
<td>2.37</td>
<td>1.45</td>
<td>(1.86)</td>
<td>(5.68)</td>
<td>1.45</td>
<td></td>
</tr>
<tr>
<td>79</td>
<td>&quot;</td>
<td>0.36</td>
<td>0.28</td>
<td>2.8</td>
<td>(0.65)</td>
<td>3.45</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>&quot;</td>
<td>0.09</td>
<td>0.11</td>
<td>0.21</td>
<td>2.28</td>
<td>1.21</td>
<td>3.49</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>102</td>
<td>&quot;</td>
<td>0.09</td>
<td>0.19</td>
<td>0.19</td>
<td>2.22</td>
<td>1.20</td>
<td>3.42</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>103</td>
<td>&quot;</td>
<td>0.11</td>
<td>0.25</td>
<td>0.19</td>
<td>2.35</td>
<td>1.12</td>
<td>3.47</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>105</td>
<td>&quot;</td>
<td>0.10</td>
<td>0.64</td>
<td>0.24</td>
<td>2.36</td>
<td>1.06</td>
<td>3.42</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>86</td>
<td>C(DNP)</td>
<td>0.14</td>
<td>0.66</td>
<td>0.44</td>
<td>(0.30)</td>
<td>2.4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>84</td>
<td>&quot;</td>
<td>0.21</td>
<td>0.75</td>
<td>(0.51)</td>
<td>0.40</td>
<td>4.65</td>
<td>(4.65)</td>
<td>1.14</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>87</td>
<td>&quot;</td>
<td>(0.30)</td>
<td>1.04</td>
<td>(0.70)</td>
<td>3.9</td>
<td>(3.90)</td>
<td>1.22</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>97</td>
<td>F(NO$_2^8$)</td>
<td>0.10</td>
<td>0.23</td>
<td>0.14</td>
<td>1.19</td>
<td>1.40</td>
<td>(0.93)</td>
<td>3.52</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>98</td>
<td>&quot;</td>
<td>0.22</td>
<td>0.21</td>
<td>1.08</td>
<td>1.28</td>
<td>1.00</td>
<td>3.36</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Average: 0.12  Varies: 0.31  0.44  1.14  1.40  1.15  1.23

Molar Ratio: 0.24  0.37  0.22  0.86  1.16  1.22  0.92
**TABLE 4.1.2.**

Reaction: CH₂ + Et O Prn at 20°C

Chromat Column: F(DNP)D

Column Temp.: 20°C

Peak areas normalized to Di n Propyl Ether

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Ketene</th>
<th>Ether</th>
<th>CH₃CHO</th>
<th>Me O Et</th>
<th>C₂H₅CHO</th>
<th>Me O Prn</th>
<th>C₆H₁₄</th>
<th>Et O Bu¹</th>
<th>Et O Bu₂sec</th>
<th>Pri O Prn</th>
<th>Et O Bu³</th>
<th>Pri O Prn</th>
</tr>
</thead>
<tbody>
<tr>
<td>64</td>
<td>2.8</td>
<td>3.8</td>
<td>0.45</td>
<td>0.14</td>
<td>(0.21)</td>
<td>0.29</td>
<td>(2.95)</td>
<td></td>
<td></td>
<td>1.32</td>
<td>1.11</td>
<td>(4.27)</td>
</tr>
<tr>
<td>106</td>
<td>3.3</td>
<td>7.7</td>
<td>0.10</td>
<td>0.47</td>
<td>0.26</td>
<td>(2.22)</td>
<td></td>
<td>1.22</td>
<td>1.19</td>
<td>3.44</td>
<td></td>
<td></td>
</tr>
<tr>
<td>107</td>
<td>3.8</td>
<td>3.9</td>
<td>0.13</td>
<td>0.37</td>
<td>0.24</td>
<td>(2.30)</td>
<td></td>
<td>1.30</td>
<td>1.22</td>
<td>3.60</td>
<td></td>
<td></td>
</tr>
<tr>
<td>108</td>
<td>4.15</td>
<td>5.7</td>
<td>0.31</td>
<td>0.31</td>
<td>0.21</td>
<td>(2.24)</td>
<td>(1.03)</td>
<td>1.17</td>
<td>(1.02)</td>
<td>3.51</td>
<td></td>
<td></td>
</tr>
<tr>
<td>109</td>
<td>3.6</td>
<td>6.7</td>
<td>0.10</td>
<td>0.47</td>
<td>0.23</td>
<td>(2.17)</td>
<td></td>
<td>1.17</td>
<td>(1.02)</td>
<td>3.51</td>
<td></td>
<td></td>
</tr>
<tr>
<td>397</td>
<td>3.2</td>
<td>4.5</td>
<td>0.12</td>
<td>0.33</td>
<td>(0.51)</td>
<td>(2.50)</td>
<td>(1.75)</td>
<td>1.11</td>
<td>(4.25)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Average:</strong></td>
<td></td>
<td></td>
<td><strong>0.38</strong></td>
<td><strong>0.11</strong></td>
<td><strong>0.38</strong></td>
<td><strong>0.25</strong></td>
<td>(Varies)</td>
<td><strong>1.25</strong></td>
<td><strong>1.16</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>(Varies)</strong></td>
<td></td>
<td></td>
<td><strong>(Varies)</strong></td>
<td></td>
<td><strong>(Varies)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Average molar ratio:

|          |        |        |        |        |        |        |        | 0.62    | 0.20      | 0.5       | 0.30     | 1.32      | 0.87      | ± 0.05    |

Accuracy: 0.03
CHAPTER 5

5.1. REACTIONS OF CH₂ WITH PriOPri

So far we have considered ethers containing 1, 2 C-H bonds, both symmetrical and asymmetrical. It was of interest also to investigate compounds containing tertiary C-H bonds. For this purpose the simplest symmetrical ether containing tertiary C-H bonds was chosen, namely, di-isopropyl ether.

The products of the gas phase reaction gave five peaks when analysed by gas chromatography on a F(DMP) column. Of the five major peaks on the chromatograms, three appeared after PriOPri and two before. Only two isopropyl butyl ether would be expected by insertion:

\[
CH_2 + PriOPri \rightarrow PriOBu^t
\]
\[
CH_2 + PriOPri \rightarrow PriOBu^s
\]

The shape of the third peak which appeared last, called "A", was distinctly different from that of the rest; it had a sharp front and was badly tailed. The tailing was thought to be due to the use of Firebrick. Therefore product analyses from next experiments were done on Celite (DNP), a less adsorptive support. Peak "A" now appeared just before PriOPri with a retention time about one third that on F(DMP) column. The product "A" was at first thought to be isobutyraldehyde or isopropyl alcohol which could have been formed from an intermediate complex by a H-shift. However chromatography of pure samples gave different retention times from that of peak "A". Thus using Celite (DNP) column the retention times were (Ch: 278) as follows:

- isobutyraldehyde b.p. 63.5°C Ret time 16.4 cm (chart)
- diisopropyl ether " 68.0°C " 7.8 " "

About 50 moles of peak "A" was therefore collected after separation on the
P(DNP) column for infra-red spectroscopic analysis. Peak A was shown to be acetone by comparison of its spectrum with that of a sample of pure acetone and with standard spectra.

It was noted that on chromatography column Celite (DNP) at 40°C, acetone by itself appeared at 17.3 cm while under identical conditions, "A" in the product appeared at 18.3 cm. However, it was shown that in the presence of other components the elution of acetone is retarded. To test this point further the products (Runs 151,153) were divided into two halves. The first half was chromatographed as such, while to the other a small volume of acetone was mixed before passing through the column. It was found that the mixture containing added acetone gave a single peak corresponding exactly to substance "A" at 18.3 cm.

5.2.1. INSERTION REACTION

The insertion reaction as already mentioned yielded two higher ethers by the attack at $^3$ C-H or at $^9$ C-H bond. Pr$^4$OBu$^8$ was predominant as would be expected since there are twelve $^9$ C-H bonds available to two $^3$ bonds. The molar ratios Pr$^4$OBu$^4$/Pr$^4$OBu$^8$ at various temperatures were measured and a complete set of data is to be found in Tables 5.1, 5.2, 5.3, 5.4, 5.5, the average values are drawn up in Table 5. At 16°C, the molar ratio of Pr$^4$OBu$^4$/Pr$^4$OBu$^8$ was 0.25. Insertion into any given tertiary C-H bond is thus 1.5 times as rapid as insertion into primary bond. It will be shown later that the abstraction of tertiary H atoms is faster than that of secondary H atoms. Table 5 also shows the average molar ratio at higher temperature when the value 0.25 falls to 0.16 at 190°C. For Runs done at 132°C, chlorobenzene was boiled in the outer jacket of the reaction vessel. After every five experiments it was changed because after exposure to U.V. it gets dark in colour.
5.2.2. Table 5.7. (Runs 304-309) gives the absolute amount of 
Pr\textsuperscript{4}OBu\textsuperscript{8} formed when air was added to the system. Here the keten and ether 
concentrations and the time of irradiation were fixed. When the molar 
quantities of Pr\textsuperscript{4}OBu\textsuperscript{8} were plotted against pressure of air, it was found 
that with the addition of air up to 2.1 cm pressure an increase in the yield 
of this ether occurred. Thereafter the yield fell slightly with up to 13 cm 
and remained constant. In contrast the yield of Pr\textsuperscript{4}OBu\textsuperscript{t} showed a continual 
fall with the increase of added air, and at 16.6 cm only a trace appeared. 
This suggests that the Pr\textsuperscript{4}OBu\textsuperscript{t} was formed in an activated state which was 
capable of reacting with oxygen.

An estimate of the difference of activation energies and the relative 
A factors for the two insertion reactions forming Pr\textsuperscript{4}OBu\textsuperscript{t} and Pr\textsuperscript{4}OBu\textsuperscript{s} by steps 
(1) and (2) below

\begin{align*}
\text{CH}_2 + \text{Pr}^4\text{OPr}^t & \xrightarrow{k_1} \text{Pr}^4\text{OBu}^t \\
\text{CH}_2 + \text{Pr}^4\text{OPr}^t & \xrightarrow{k_2} \text{Pr}^4\text{OBu}^s
\end{align*}

can be made by plotting the product ratio \( \frac{\text{Pr}^4\text{OBu}^t}{\text{Pr}^4\text{OBu}^s} \) against \( \frac{1}{T} \).

This gives \( E_2 - E_1 = 0.9 \text{ kcal mole}^{-1}, A_1/A_2 = 0.053 \). The relative A factors 
for individual C-H bond is \( A_1/A_2 = 0.31 \). The effect of \( E \) and A factors thus 
tend to cancel out.

5.3.1. DISPLACEMENT REACTION

The attack of methylene on Pr\textsuperscript{4}OPr\textsuperscript{i} also gave methyl isopropyl ether 
by the Displacement reaction observed in the previous work

\[ \text{CH}_2 + \text{Pr}^4\text{OPr}^i \rightarrow \text{MeOPr}^i + \text{C}_3\text{H}_6 \]

Methyl isopropyl ether was identified by its retention time. At room temperature 
the relative rate of formation of this ether was 0.13. At 68.7 and 190°C the
relative rate was 0.09 (Table 5). The detailed data will be found in Tables 5.1 to 5.8. The other product of the reaction, propylene, was determined on an adsorption column.

The propylene was determined at two temperatures, 100°C and 132°C, using a combined system of columns (details given later) where acetone could be best separated instead of Pr\textsuperscript{1}OBu\textsubscript{8} (Tables 5.9.1, 5.9.2). However, propylene also arises by the disproportionation of propyl radicals released by the abstraction reaction which is responsible for the production of acetone. The formation of C\textsubscript{3}H\textsubscript{6} is therefore no proof of the occurrence of the insertion reaction.

5.4.1. ABSTRACTION REACTION

Methylene has been found to abstract tertiary hydrogen from the isopropyl group of Pr\textsuperscript{1}OPr\textsuperscript{i}. This reaction is about 13 times faster than the abstraction of secondary hydrogen from diethyl ether.

The abstraction reaction gives rise to acetone and lower hydrocarbons which are formed as a result of free radical reactions. The lower hydrocarbons found were methane, ethane, propane, propylene, 2,3 dimethyl butane and isobutane. Of these, methane was not measured quantitatively as it was by far the smallest in amount. The relative yield of ethane, propane, propylene, and isobutane have been determined using combined column and their yields, normalized to acetone, are given in Table 5.9.2. The relative yields of 2,3, dimethyl butane (biisopropyl) was found using celite column and the values normalized to Pr\textsuperscript{1}OBu\textsubscript{8} are given in Tables 5.1 to 5.7. The following mechanism is proposed for the products resulting from the abstraction reaction:

\[
\begin{align*}
\text{CH}_2 + (\text{CH}_3)_2\text{CHOCH(CH}_3)_2 & \xrightarrow{k_1} \text{CH}_3 + \text{iso-C}_3\text{H}_7\text{COCH}_3 \quad \ldots \ldots \ldots (1) \\
\text{iso-C}_3\text{H}_7\text{COCH}_3 & \xrightarrow{k_2} (\text{CH}_3)_2\text{CO} + \text{iso-C}_3\text{H}_7 \quad \ldots \ldots \ldots (2) \\
2(\text{iso-C}_3\text{H}_7) & \xrightarrow{k_3} (\text{CH}_3)_2\text{CHCH(CH}_3)_2 \quad \ldots \ldots \ldots (3)
\end{align*}
\]
\[2(\text{iso-}C_3H_7) \xrightarrow{k_4} C_3H_6 + C_3H_8 \cdots \cdots \cdots \] (4)
\[\cdot CH_3 + \text{iso-}C_3H_7 \xrightarrow{k_5} (C_3H_6 + CH_4) \text{ or } \text{iso } C_4H_{10} \cdots \] (5)
\[\cdot CH_3 + \cdot CH_3 \xrightarrow{k_6} C_2H_6 \cdots \cdots \cdots \] (6)

Owing to the high activation energies of abstraction by monoradicals (7-10 keals) no further abstraction is likely at 20°C. The iso-C_3H_7O(CH_3)_2 radical apparently decomposes readily into acetone and an isopropyl radical. Recombination of isopropyl and methyl by steps (3), (5), (6) results in the formation of 2,3-dimethyl butane, isobutane and ethane found in the products. The propylene and propane obtained in the products arise from mixed disproportionation (step (4)), a process which competes with step 3 and is faster than the latter. The recombination of the free radicals has almost no activation energy and therefore considerable amounts of these products are formed. 2,3-dimethyl butane formed from (3) increases many times from a temperature of 68.7°C to 190°C. Though Table 5.9 gives values for ethane, propane, propylene, and isobutane at 100°C, it seems likely that at higher temperatures these will be high too. The fact that C_3H_6 is not equimolar in amount to propane is because of the contribution of step (5) and of the displacement reaction.

If the above mechanism is correct then acetone and lower hydrocarbons must be produced in equivalent amount viz. the yields of acetone and hydrocarbons should be related by the equation

\[
2 \left[ \frac{\text{Pr}^1\text{Pr}^1}{\text{Acetone}} \right] + \left[ \frac{\text{Propane}}{\text{Acetone}} \right] + \left[ \frac{\text{Propylene}}{\text{Acetone}} \right] + \left[ \frac{\text{iso-butane}}{\text{Acetone}} \right] = 1.00
\]

where \[\text{propylene}\] is the experimental yield less the \[\text{propylene}\] from displacement reaction. From Fig.11 we find interpolation the value for biisopropyl at 100°C to be 1.06 and hence Biisopropyl/\text{Acetone} = 0.11. From Table 5.9.2 we have the average molar ratio of the other products.
The table above proves within experimental limits of error the authenticity of the proposed mechanism. Only the abstraction of tertiary hydrogen leads to acetone formation and the formation of an approximately equimolar amount of hydrocarbons shows that abstraction of primary atoms is likely to be unimportant.

5.4.2. THE ANALYSIS OF LOWER HYDROCARBONS

The quantitative measurement of hydrocarbons referred to above was based on acetone as the standard. For this purpose chromatography systems consisted of a combination of partition column No.5 (Table 1) and an adsorption column No.12 (Table 2). The 'split-column' is shown diagrammatically in Fig.14. The products to be separated were passed into the alumina column via the F(DMP) for long enough to elute the hydrocarbons completely from the latter so that they were now adsorbed on the alumina column. The carrier gas was diverted so that it by-passed the alumina and thus ethers and acetone were eluted first from F(DMP). Then the lower hydrocarbons were eluted from the alumina column. Reproducibility was poor and the separation of isobutane from propylene was sometimes incomplete.
The procedure was modified by connecting the two columns in parallel and by maintaining both at about 40°C. To obtain adequate amounts of products runs were carried out at 100°C in view of the four-fold increase in acetone compared to 16°C runs. From the reaction vessel, the products were expanded into the short line (A), after which C was closed. Part of products in the line A were analysed on F(DMP), and the remaining part in the reaction vessel called B, was analysed on alumina for lower hydrocarbons. The ratio of the volume of A to B was 0.90 and has been used in computing data given in Table 5.9. The average peak area ratios have been converted to molar ratio by applying the sensitivity correction from Table 2. Propylene is the major fraction, followed in quantity by iso-butane, and by propane. The values based on acetone yield have been converted to \(Pr^I\)Obu\(^8\) basis by applying a correction factor 1.19, being the molar ratio of acetone/\(Pr^I\)Obu\(^8\) at 100°C.

5.4.3. TEMPERATURE DEPENDANCE OF THE ABSTRACTION REACTION

In view of the large variation in the relative molar yield of acetone with temperature the activation energy differences between the abstraction and insertion reaction was calculated

\[
\begin{align*}
\text{CH}_2 + (\text{iso-C}_3\text{H}_7)_2\text{O} & \xrightarrow{k_1} (\text{CH}_3)_2\text{CO} + \text{lower hydrocarbons} \\
\text{CH}_2 + (\text{iso-C}_3\text{H}_7)_2\text{O} & \xrightarrow{k_2} \text{Pr}^I\text{Obu}^8
\end{align*}
\]

Then \(R_{\text{acetone}} = k_1 \left[ \frac{\text{CH}_2}{[\text{Pr}^I\text{OBu}^8]} \right] \)

and \(R_{\text{Pr}^I\text{Obu}^8} = k_2 \left[ \frac{\text{CH}_2}{[\text{Pr}^I\text{OBu}^8]} \right] \)

Therefore \(R_{\text{acetone}}/R_{\text{Pr}^I\text{Obu}^8} = k_1/k_2 \) which is known from the relative rate of acetone formation at different temperatures. An Arrhenius plot of these values is shown in Fig. 12, from which \(E_1 - E_2 = 3.8 \text{ kilocalories/mole} \) and the 
\(A_1/A_2 = 1.32 \times 10^2.\)
Since the rate of H-abstraction increased at higher temperatures, the production of methyl and iso-propyl radicals also must increase. The chromatographic system was such that all the ethers and acetone could be analysed directly. However, only for the set of experiments reported above were the lower hydrocarbons simultaneously determined. Nevertheless, as is clear from Table 5.9, the recombination

\[
\text{iso-C}_3\text{H}_7 + \text{iso-C}_3\text{H}_7 \rightarrow \text{Bi iso-propyl}
\]

increases as the reaction temperature is increased. The increase is gradual from 68.7°C to 132°C but more marked at higher temperature. As these reactions are closely connected with those giving other hydrocarbons, it is very likely that their relative rates are affected in a similar manner.

5.4.4. EFFECT OF CARBON DIOXIDE.

The addition of carbon dioxide to the system at room temperature (Table 5.8), and at 132°C (Table 5.6), was studied. In both the Tables it will be noted that many of the values for bi-isopropyl are missing, the reason being that when large quantities of CO₂ were added, the products after the reaction were condensed in liquid oxygen, carbon dioxide could not be pumped off with uncondensable gases. Consequently in the chromatograms there appeared a large negative peak just before bi-isopropyl peak whose estimation was often in error, if not impossible. The negative peak was found to be caused by the sudden build-up of pressure when the frozen carbon dioxide and products were warmed for injection from the 'U' trap (Fig.1). This resulted in the 'blow-back' of carbon dioxide which inadvertently carried a small fraction of products via the balancing side of the conductivity gauge. Subsequently a trap containing KOH pellets was used as absorbent for the excess carbon dioxide.

In experiments done at 16°C and 132°C the results are reported
in Tables 5.3 and 5.6. At 16°C the relative yield of lower ether MeOPri shows a fall and is 0.06 with a CO₂ concentration of 36.4 cm, compared with 0.13 in the absence of CO₂. The relative yield of Pr⁻OBu⁺, on the other hand, shows a small increase, being 0.32 on an average in the presence of 32–37 cm CO₂ compared to 0.25 in the absence of CO₂. The relative yield of acetone likewise showed a rise from 0.22 to 0.40 for runs done at 16°C although at small CO₂ pressures as also at higher temperature it decreased slightly. At 132°C the relative yield of bi-isopropyl again shows an increase from 0.17 to 0.21 in the presence of CO₂.

5.4.5. EFFECT OF OXYGEN

It being known from the studies in Chapter 3 that the products of abstraction reaction acetaldehyde increases greatly on addition of oxygen (air) to the system, similar studies were made with Pr⁻OPri. The reaction of methylene with Pr⁻OPri at 132°C was investigated. Random pressure of air added were chosen and up to about 23 cm air was introduced to the system. Acetone (product of abstraction reaction) was found to increase manifoldly with the increase in oxygen to the system. The complete set of data is given in Table 5.7 and when these values were plotted against the air pressure marked rise in the curve was obtained, similar to the one obtained for acetaldehyde in Fig.6. The value for Run 275, being in error, is bracketed in Table 5.7 where Runs 304-309 were made when keten and ether concentration were fixed at 2:8.

The values for the relative yield of bi-isopropyl ether are much lower (Runs 304,305) than the corresponding figure of 0.17 in the absence of air, although at low air pressures (Runs 308, 309, 254) both acetone and Bi-Pr⁺ show an increase. The fall in bi-isopropyl is presumably due to the oxidation
of isopropyl radicals before they can dimerise. Reaction 4-6 may occur

\[ \text{isoC}_3\text{H}_7 + \text{O}_2 \xrightarrow{k_4} \text{isoC}_3\text{H}_7\text{OO} \]

\[ \text{iso-C}_2\text{H}_2 \text{O} \xrightarrow{k_5} \text{CH}_3 \cdot \text{O}=\text{O} + \text{OH} \]

\[ (\text{iso-C}_3\text{H}_7)_2 \text{O} + \text{OH} \xrightarrow{k_6} \text{iso-C}_3\text{H}_7\text{O}^=\text{C}_3\text{H}_6 \]

Isopropyl radical may give rise to acetone according to steps (4) and (5).

The activation energy for

\[ \text{CH}_3 + \text{O}_2 \rightarrow \cdot \text{CHO} + \text{H}_2\text{O} \]

has been estimated by Van Tiggelen\(^2\) from the oxidation of methane photosensitised by acetone to be \(1.5 \text{ kcal} \). Steacie\(^3\) estimated it to be \(\sim 0\).

It seems unlikely that \(E_4\) will be much higher than \(1 \text{ kcal}\) or so as it is similar to that of (7). A high proportion of iso-\(\text{C}_3\text{H}_7\) radicals should be oxidised in the presence of oxygen. The great increase in the yield of acetone (more than five times) suggests that short chains can occur in the presence of oxygen and that much more reactive radicals than CH\(_3\) must be formed. OH is the most obvious choice although there is no direct evidence for reaction 5. Isobutane is largely a product of recombination of isopropyl and methyl radicals generated in the system and falls considerably with the addition of air (Table 5.9.1, 5.9.2). Here propylene shows a similar trend and is expected in view of the fact that the radicals are getting readily oxidised.

The effect of oxygen on the products of insertion reaction, MeOPri\(^1\) and PriOBu\(^1\) at 132°C can be found in Table 5.7. The molar rate of formation of MeOPri\(^1\) at 132°C shows no change on the addition of air up to 22.9 cm (Run 275). On an average a value of 0.09 compared to 0.08 in the absence of air is obtained. The relative rate of PriOBu\(^1\) shows a steady fall, it being negligible at an air pressure of 16.6 cm (Run 307).
### TABLE 5

Average values for products normalized to Pr^1OBu^6

Reaction: Methylene with diisopropyl ether.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Biisopropyl</th>
<th>MeOPri</th>
<th>Pr^1OBu</th>
<th>Acetone</th>
</tr>
</thead>
<tbody>
<tr>
<td>16°C</td>
<td>nil</td>
<td>0.13</td>
<td>0.25</td>
<td>0.22</td>
</tr>
<tr>
<td>68.7°C</td>
<td>0.07</td>
<td>0.09</td>
<td>0.18</td>
<td>0.72</td>
</tr>
<tr>
<td>100°C</td>
<td>-</td>
<td>0.09</td>
<td>0.17</td>
<td>1.19</td>
</tr>
<tr>
<td>132°C</td>
<td>0.17</td>
<td>0.08</td>
<td>0.16</td>
<td>1.86</td>
</tr>
<tr>
<td>190°C</td>
<td>0.43</td>
<td>0.09</td>
<td>0.15</td>
<td>3.30</td>
</tr>
</tbody>
</table>

**Effect of Carbon Dioxide:**

At 132°C with

Added CO₂

(0.5 - 36 cm Hg)

- 0.28
- 0.06
- 0.16

Varies with CO₂

**Accuracy of Results**

- Table 5.1.1. (16°C) ±0.02 ±0.02
- Table 5.2. (68°C) ±0.003 ±0.03
- Table 5.3. (100°C) n ±0.03
- Table 5.6. (132°C) ±0.003 ±0.025
Irradiation: Ketene + Di-IP Ether at 16°C.
Column: F(DMP) double
N₂ flow: 16 c.c.s/mt.
R.V.: 30 mls. capacity

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Ketene P cm</th>
<th>Ether P cm</th>
<th>Duration of run Hr.-mts.</th>
<th>MeOPri</th>
<th>PriOBu²</th>
<th>PriOBu⁵</th>
<th>Acetone</th>
</tr>
</thead>
<tbody>
<tr>
<td>129</td>
<td>6.7</td>
<td>7.9</td>
<td>2-50</td>
<td>2.48</td>
<td>7.3</td>
<td>33.0</td>
<td></td>
</tr>
<tr>
<td>130</td>
<td>10.5</td>
<td>8.0</td>
<td>3-30</td>
<td>2.73</td>
<td>8.78</td>
<td>40.4</td>
<td>2.9</td>
</tr>
<tr>
<td>131</td>
<td>5.8</td>
<td>7.6</td>
<td>1-20</td>
<td>2.0</td>
<td>6.48</td>
<td>33.2</td>
<td>2.25</td>
</tr>
<tr>
<td>138</td>
<td>3.0</td>
<td>6.4</td>
<td>2-45</td>
<td>8.2</td>
<td>28.5</td>
<td>112.6</td>
<td>18.5</td>
</tr>
<tr>
<td>139</td>
<td>2.5</td>
<td>5.0</td>
<td>1-20</td>
<td>3.5</td>
<td>6.4</td>
<td>23.1</td>
<td>5.3</td>
</tr>
<tr>
<td>140</td>
<td>2.1</td>
<td>5.5</td>
<td>0-50</td>
<td>4.16</td>
<td>10.76</td>
<td>37.3</td>
<td>8.8</td>
</tr>
<tr>
<td>155</td>
<td>1.1</td>
<td>2.1</td>
<td>0-12</td>
<td>0.9</td>
<td>4.6</td>
<td>12.9</td>
<td></td>
</tr>
</tbody>
</table>

(Peak Areas Normalized to PriOBu⁵)

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Ketene P cm</th>
<th>Ether P cm</th>
<th>Duration of run Hr.-mts.</th>
<th>MeOPri</th>
<th>PriOBu²</th>
<th>PriOBu⁵</th>
<th>Acetone</th>
</tr>
</thead>
<tbody>
<tr>
<td>227</td>
<td>2.0</td>
<td>6.8</td>
<td>2-50</td>
<td>7.6</td>
<td>18.3</td>
<td>63.6</td>
<td>19.0</td>
</tr>
<tr>
<td>228</td>
<td>2.2</td>
<td>8.2</td>
<td>1-20</td>
<td>13.0</td>
<td>43.8</td>
<td>190.4</td>
<td>33.8</td>
</tr>
<tr>
<td>229</td>
<td>1.6</td>
<td>8.3</td>
<td>2-45</td>
<td>7.2</td>
<td>31.6</td>
<td>120.2</td>
<td>22.6</td>
</tr>
<tr>
<td>230</td>
<td>2.0</td>
<td>8.0</td>
<td>1-20</td>
<td>10.0</td>
<td>27.1</td>
<td>101.3</td>
<td>18.0</td>
</tr>
<tr>
<td>265</td>
<td>1.4</td>
<td>6.8</td>
<td>1-5</td>
<td>9.6</td>
<td>36.8</td>
<td>143.8</td>
<td>17.3</td>
</tr>
</tbody>
</table>

(Columns: Celite(DNP) single)
(N₂ flow: 7 c.c.s/mt.)

For Check: Celite (S) N₂ flow: 9 c.c.s/mt.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Ketene P cm</th>
<th>Ether P cm</th>
<th>Duration of run Hr.-mts.</th>
<th>MeOPri</th>
<th>PriOBu²</th>
<th>PriOBu⁵</th>
<th>Acetone</th>
</tr>
</thead>
<tbody>
<tr>
<td>364</td>
<td>2.3</td>
<td>5.7</td>
<td>2-00</td>
<td>0.08</td>
<td>0.22</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Average of all Runs (except values in brackets):

Molar Ratios:

Accuracy:
<table>
<thead>
<tr>
<th>Run No.</th>
<th>Ketene P cm</th>
<th>Ether P cm</th>
<th>C.T. °C</th>
<th>Duration of run Hr mts.</th>
<th>Peak Areas MeOPr₁</th>
<th>Pr¹OBu</th>
<th>Pr¹OBu sec.</th>
<th>Acetone</th>
<th>Normalized to Pr¹OBu sec. MeOPr₁</th>
<th>Pr¹OBu</th>
<th>Acetone</th>
</tr>
</thead>
<tbody>
<tr>
<td>199</td>
<td>2.2</td>
<td>7.2</td>
<td>39</td>
<td>1 - 30</td>
<td>3.2</td>
<td>10.5</td>
<td>56.8</td>
<td>14.3</td>
<td>0.06</td>
<td>0.19</td>
<td>(0.25)</td>
</tr>
<tr>
<td>200</td>
<td>3.8</td>
<td>6.3</td>
<td>39.2</td>
<td>2 - 0</td>
<td>5.98</td>
<td>18.5</td>
<td>76.9</td>
<td>37.9</td>
<td>0.08</td>
<td>0.24</td>
<td>0.49</td>
</tr>
<tr>
<td>201</td>
<td>2.8</td>
<td>8.4</td>
<td>37.3</td>
<td>3 - 0</td>
<td>5.7</td>
<td>17.4</td>
<td>78.8</td>
<td>38.1</td>
<td>0.07</td>
<td>0.22</td>
<td>0.48</td>
</tr>
<tr>
<td>202</td>
<td>2.0</td>
<td>7.1</td>
<td>35</td>
<td>2 - 0</td>
<td>4.4</td>
<td>12.7</td>
<td>64.9</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Celite (S) Column
N₂ flow: 12 c.c.s/mt.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Ketene P cm</th>
<th>Ether P cm</th>
<th>C.T. °C</th>
<th>Duration of run Hr mts.</th>
<th>Peak Areas MeOPr₁</th>
<th>Pr¹OBu</th>
<th>Pr¹OBu sec.</th>
<th>Acetone</th>
<th>Normalized to Pr¹OBu sec. MeOPr₁</th>
<th>Pr¹OBu</th>
<th>Acetone</th>
</tr>
</thead>
<tbody>
<tr>
<td>203</td>
<td>2.2</td>
<td>8.5</td>
<td>36</td>
<td>1 - 30</td>
<td>4.98</td>
<td>14.3</td>
<td>86.2</td>
<td>41.1</td>
<td>0.06</td>
<td>0.17</td>
<td>0.48</td>
</tr>
<tr>
<td>204</td>
<td>3.0</td>
<td>5.8</td>
<td>31</td>
<td>1 - 0</td>
<td>8.9</td>
<td>5.7</td>
<td>17.9</td>
<td>107.4</td>
<td>0.06</td>
<td>0.17</td>
<td>0.52</td>
</tr>
<tr>
<td>205</td>
<td>2.0</td>
<td>4.85</td>
<td>31.3</td>
<td>1 - 45</td>
<td>7.86</td>
<td>2.98</td>
<td>5.05</td>
<td>29.5</td>
<td>0.06</td>
<td>0.18</td>
<td>(0.60)</td>
</tr>
<tr>
<td>206</td>
<td>1.6</td>
<td>7.0</td>
<td>30.3</td>
<td>1 - 30</td>
<td>-</td>
<td>5.8</td>
<td>18.3</td>
<td>102.8</td>
<td>0.06</td>
<td>0.18</td>
<td>(0.60)</td>
</tr>
<tr>
<td>207</td>
<td>1.5</td>
<td>5.4</td>
<td>32.3</td>
<td>1 - 30</td>
<td>5.25</td>
<td>15.6</td>
<td>91.6</td>
<td>57.2</td>
<td>0.06</td>
<td>0.17</td>
<td>0.48</td>
</tr>
</tbody>
</table>

Average of all runs except) those values which are in ) =
Molar Ratios: 0.09 0.18 0.72
Accuracy: 0.003 +0.03
TABLE 5.3

Irradiation: Ketene + Di isopropyl Ether at 100°C
Column : F(DMP) double
N₂ flow : 16 c.c./mt.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Ketene P cm</th>
<th>Ether P cm</th>
<th>C.T. °C</th>
<th>Duration of Run</th>
<th>BiPr⁺</th>
<th>MeOPr⁺</th>
<th>PriOBu⁺</th>
<th>PriOBu⁻</th>
<th>Acetone</th>
</tr>
</thead>
<tbody>
<tr>
<td>132</td>
<td>6.2</td>
<td>6.0</td>
<td>46.5</td>
<td>2-0</td>
<td>0.9</td>
<td>2.8</td>
<td>17.73</td>
<td>10.2</td>
<td></td>
</tr>
<tr>
<td>133</td>
<td>8.9</td>
<td>7.6</td>
<td>47.3</td>
<td>3-0</td>
<td>1.10</td>
<td>3.89</td>
<td>20.2</td>
<td>13.83</td>
<td></td>
</tr>
<tr>
<td>134</td>
<td>17.4</td>
<td>6.7</td>
<td>48.3</td>
<td>1-30</td>
<td>0.96</td>
<td>2.92</td>
<td>17.4</td>
<td>11.72</td>
<td></td>
</tr>
<tr>
<td>141</td>
<td>2.3</td>
<td>4.4</td>
<td>40.8</td>
<td>0-50</td>
<td>4.9</td>
<td>2.64</td>
<td>19.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>142</td>
<td>2.0</td>
<td>6.2</td>
<td>41.3</td>
<td>0-50</td>
<td>1.3</td>
<td>5.15</td>
<td>31.7</td>
<td>20.88</td>
<td></td>
</tr>
<tr>
<td>143</td>
<td>4.4</td>
<td>7.3</td>
<td>39.3</td>
<td>1-0</td>
<td>3.5</td>
<td>8.78</td>
<td>58.3</td>
<td>43.56</td>
<td></td>
</tr>
<tr>
<td>144</td>
<td>3.5</td>
<td>8.1</td>
<td>39.0</td>
<td>2-0</td>
<td>3.5</td>
<td>10.5</td>
<td>53.8</td>
<td>50.6</td>
<td></td>
</tr>
<tr>
<td>145</td>
<td>2.4</td>
<td>9.3</td>
<td>40.0</td>
<td>1-30</td>
<td>4.1</td>
<td>8.63</td>
<td>45.26</td>
<td>42.74</td>
<td></td>
</tr>
<tr>
<td>156</td>
<td>2.4</td>
<td>6.9</td>
<td>37.0</td>
<td>0-40</td>
<td>4.27</td>
<td>2.4</td>
<td>19.3</td>
<td>15.6</td>
<td></td>
</tr>
<tr>
<td>157</td>
<td>2.2</td>
<td>6.6</td>
<td>40.0</td>
<td>2-17</td>
<td>3.0</td>
<td>6.84</td>
<td>48.0</td>
<td>34.2</td>
<td></td>
</tr>
<tr>
<td>158</td>
<td>2.2</td>
<td>7.8</td>
<td>40.0</td>
<td>2-0</td>
<td>1.97</td>
<td>4.99</td>
<td>32.5</td>
<td>33.9</td>
<td></td>
</tr>
</tbody>
</table>

Normalized to Pr³OBu⁻

<table>
<thead>
<tr>
<th>BiPr⁺</th>
<th>PriOMe</th>
<th>PriOBu⁻</th>
<th>Acetone</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05</td>
<td>0.18</td>
<td>0.57</td>
<td></td>
</tr>
<tr>
<td>0.05</td>
<td>0.19</td>
<td>0.68</td>
<td></td>
</tr>
<tr>
<td>0.06</td>
<td>0.17</td>
<td>0.67</td>
<td></td>
</tr>
<tr>
<td>(0.51)</td>
<td>(0.22)</td>
<td>(0.20)</td>
<td></td>
</tr>
<tr>
<td>(0.42)</td>
<td>0.16</td>
<td>0.66</td>
<td></td>
</tr>
<tr>
<td>0.06</td>
<td>0.15</td>
<td>0.75</td>
<td></td>
</tr>
<tr>
<td>0.06</td>
<td>0.20</td>
<td>0.94</td>
<td></td>
</tr>
<tr>
<td>0.09</td>
<td>0.19</td>
<td>0.94</td>
<td></td>
</tr>
<tr>
<td>0.06</td>
<td>0.12</td>
<td>0.86</td>
<td></td>
</tr>
<tr>
<td>0.06</td>
<td>0.14</td>
<td>0.71</td>
<td></td>
</tr>
<tr>
<td>0.06</td>
<td>0.15</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

Average of all (Runs) values except those in brackets.

Accuracy of the Results:

±0.003 ±0.03
### Table 5.4

**Irradiation: Ketene + Di iPr Ether at 132°C**

- **Column:** Celite (S)
- **N₂ flow:** 10 c.c./min.

#### PEAK AREAS

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Ketene P cm</th>
<th>Ether P cm</th>
<th>C.T.</th>
<th>Duration of Run</th>
<th>Bi Pr¹</th>
<th>Me O Pr¹</th>
<th>Pr¹ O Bu¹</th>
<th>Pr¹OBU¹</th>
<th>Acetone</th>
</tr>
</thead>
<tbody>
<tr>
<td>208</td>
<td>1.8</td>
<td>6.9</td>
<td>32°C</td>
<td>21°C</td>
<td>7.1</td>
<td>2.9</td>
<td>8.0</td>
<td>54.6</td>
<td>63.8</td>
</tr>
<tr>
<td>209</td>
<td>2.0</td>
<td>5.4</td>
<td>21°C</td>
<td>20°C</td>
<td>5.68</td>
<td>0.56</td>
<td>2.7</td>
<td>-</td>
<td>4.5</td>
</tr>
<tr>
<td>210</td>
<td>1.7</td>
<td>7.1</td>
<td>20°C</td>
<td>2-30</td>
<td>5.4</td>
<td></td>
<td></td>
<td>24.5</td>
<td></td>
</tr>
<tr>
<td>211</td>
<td>2.0</td>
<td>4.8</td>
<td>25°C</td>
<td></td>
<td>13.2</td>
<td>2.5</td>
<td>5.8</td>
<td>43.1</td>
<td>66.2</td>
</tr>
<tr>
<td>212</td>
<td>1.9</td>
<td>6.5</td>
<td>46°C</td>
<td></td>
<td>3.7</td>
<td>1.0</td>
<td></td>
<td>24</td>
<td>33.0</td>
</tr>
<tr>
<td>213</td>
<td>1.5</td>
<td>6.3</td>
<td>48°C</td>
<td></td>
<td>3.8</td>
<td></td>
<td></td>
<td>21.9</td>
<td></td>
</tr>
<tr>
<td>214</td>
<td>2.1</td>
<td>6.1</td>
<td>36°C</td>
<td></td>
<td>4.2</td>
<td></td>
<td></td>
<td>11.3</td>
<td>17.9</td>
</tr>
<tr>
<td>215</td>
<td>1.7</td>
<td>6.9</td>
<td>34°C</td>
<td></td>
<td></td>
<td></td>
<td>2.4</td>
<td>17.5</td>
<td>20.5</td>
</tr>
<tr>
<td>216</td>
<td>2.7</td>
<td>6.4</td>
<td>32°C</td>
<td></td>
<td>5.45</td>
<td>2.1</td>
<td>6.16</td>
<td>45.5</td>
<td>51.0</td>
</tr>
<tr>
<td>217</td>
<td>2.7</td>
<td>7.0</td>
<td>32°C</td>
<td></td>
<td>9.5</td>
<td>2.56</td>
<td>9.15</td>
<td>55.5</td>
<td>61.2</td>
</tr>
<tr>
<td>218</td>
<td>1.8</td>
<td>8.0</td>
<td>23°C</td>
<td>-</td>
<td>2.6</td>
<td>9.0</td>
<td>52.5</td>
<td>(63)</td>
<td></td>
</tr>
<tr>
<td>219</td>
<td>1.7</td>
<td>9.8</td>
<td>26°C</td>
<td></td>
<td>16.2</td>
<td>2.8</td>
<td>6.7</td>
<td>50.5</td>
<td></td>
</tr>
<tr>
<td>220</td>
<td>1.6</td>
<td>6.7</td>
<td>30°C</td>
<td></td>
<td>(8.5)</td>
<td>4.0</td>
<td>25.2</td>
<td>32.7</td>
<td>(0.34)</td>
</tr>
<tr>
<td>221</td>
<td>1.7</td>
<td>8.1</td>
<td>30°C</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Ketene P cm</th>
<th>Ether P cm</th>
<th>C.T.</th>
<th>Duration of Run</th>
<th>Pr¹ O Bu⁺</th>
<th>Me O Pr⁺</th>
<th>Bi Pr⁺</th>
<th>Acetone</th>
</tr>
</thead>
<tbody>
<tr>
<td>236</td>
<td>1.6</td>
<td>10.7</td>
<td>25°C</td>
<td>25°C</td>
<td>7.0</td>
<td>3</td>
<td>3.75</td>
<td>26.6</td>
</tr>
<tr>
<td>249</td>
<td>2.5</td>
<td>10.35</td>
<td>21°C</td>
<td>21°C</td>
<td>14.2</td>
<td>2.1</td>
<td>9.2</td>
<td>50.6</td>
</tr>
<tr>
<td>251</td>
<td>1.9</td>
<td>7.55</td>
<td>25°C</td>
<td>25°C</td>
<td>6.3</td>
<td>2.15</td>
<td>7.44</td>
<td>45.4</td>
</tr>
<tr>
<td>252</td>
<td>1.4</td>
<td>7.1</td>
<td>25°C</td>
<td>25°C</td>
<td>6.8</td>
<td>1.7</td>
<td>4.46</td>
<td>22.9</td>
</tr>
<tr>
<td>253</td>
<td>1.6</td>
<td>8.35</td>
<td>24°C</td>
<td>24°C</td>
<td>8.9</td>
<td>1.6</td>
<td>4.84</td>
<td>29</td>
</tr>
</tbody>
</table>

**Average:**

(excludes values inside the brackets)

**Molar Ratios:**

- Bi Pr⁺: 0.22
- Me O Pr⁺: 0.05
- Pr¹ O Bu⁺: 0.16
- Acetone: 1.17

- Acetone: 1.86
TABLE 5.5

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Ketene cm</th>
<th>Ether cm</th>
<th>C.T.</th>
<th>Duration of Run</th>
<th>PEAK AREAS</th>
<th>Values Normalized to Pr\textsuperscript{4}OBu\textsuperscript{8}</th>
<th>Molar Ratios</th>
<th>Accuracy limits</th>
</tr>
</thead>
<tbody>
<tr>
<td>232</td>
<td>2.4</td>
<td>10</td>
<td>19\degree</td>
<td></td>
<td>13.8</td>
<td>1.4</td>
<td>0.55</td>
<td>±0.01</td>
</tr>
<tr>
<td>233</td>
<td>1.4</td>
<td>7.7</td>
<td>21.3\degree</td>
<td></td>
<td>15.8</td>
<td>2.1</td>
<td>0.58</td>
<td>±0.017</td>
</tr>
<tr>
<td>234</td>
<td>1.6</td>
<td>9.0</td>
<td>21\degree</td>
<td></td>
<td>7.3</td>
<td>0.9</td>
<td>0.61</td>
<td>±0.006</td>
</tr>
<tr>
<td>235</td>
<td>1.6</td>
<td>6.6</td>
<td>24\degree</td>
<td></td>
<td>16.4</td>
<td>2.3</td>
<td>0.57</td>
<td>±0.01</td>
</tr>
</tbody>
</table>

Average of values (except those in brackets):-

<table>
<thead>
<tr>
<th>PEAK AREAS</th>
<th>Values Normalized to Pr\textsuperscript{4}OBu\textsuperscript{8}</th>
<th>Molar Ratios</th>
<th>Accuracy limits</th>
</tr>
</thead>
<tbody>
<tr>
<td>BiPr\textsuperscript{1}</td>
<td>MeOPr\textsuperscript{1}</td>
<td>Pr\textsuperscript{1}OBu\textsuperscript{8}</td>
<td>Pr\textsuperscript{1}OBu\textsuperscript{8}</td>
</tr>
<tr>
<td>0.57</td>
<td>0.06</td>
<td>0.16</td>
<td>2.31</td>
</tr>
<tr>
<td>0.43</td>
<td>0.09</td>
<td>0.15</td>
<td>3.30</td>
</tr>
<tr>
<td>±0.01</td>
<td>±0.017</td>
<td>±0.006</td>
<td></td>
</tr>
<tr>
<td>Run No.</td>
<td>Ketene P cm</td>
<td>Ether P cm</td>
<td>C.T.</td>
</tr>
<tr>
<td>--------</td>
<td>-------------</td>
<td>------------</td>
<td>------</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>237</td>
<td>1.5</td>
<td>8.2</td>
<td>26°C</td>
</tr>
<tr>
<td>238</td>
<td>1.4</td>
<td>8.5</td>
<td>26.5°C</td>
</tr>
<tr>
<td>239</td>
<td>2.2</td>
<td>7.0</td>
<td>26.7°C</td>
</tr>
<tr>
<td>240</td>
<td>2.2</td>
<td>8.75</td>
<td>26.3°C</td>
</tr>
<tr>
<td>241</td>
<td>2.3</td>
<td>10.5</td>
<td>26°C</td>
</tr>
<tr>
<td>242</td>
<td>1.8</td>
<td>9.7</td>
<td>25°C</td>
</tr>
<tr>
<td>243</td>
<td>2.0</td>
<td>8.1</td>
<td>23.3°C</td>
</tr>
<tr>
<td>244</td>
<td>2.1</td>
<td>8.8</td>
<td>25.3°C</td>
</tr>
<tr>
<td>257</td>
<td>2.0</td>
<td>8.2</td>
<td>25°C</td>
</tr>
<tr>
<td>258</td>
<td>2.0</td>
<td>8.2</td>
<td>25°C</td>
</tr>
</tbody>
</table>

Average Values: 0.04  0.28  0.16  Varies
Molar Ratios: 0.06  0.21  0.16
Accuracy of Results: ±0.003  ±0.025
**EFFECT OF OXYGEN**

Irradiation: Ketene + DiIIP Ether at 132°C

Column: Celite (DNP) single

N₂ flow: 10 c.c.s./mt.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Ketene (P cm)</th>
<th>Ether (P cm)</th>
<th>Air (P cm)</th>
<th>C.T.</th>
<th>MeOPri</th>
<th>BiPri</th>
<th>PriOBu₂</th>
<th>PriOBu₃</th>
<th>Acetone</th>
<th>Normalised to PriOBu₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>250</td>
<td>2.4</td>
<td>10.3</td>
<td>0.3</td>
<td>24.5</td>
<td>3.45</td>
<td>11.9</td>
<td>9.7</td>
<td>73.1</td>
<td>83.9</td>
<td>0.05 0.16 0.13 1.48</td>
</tr>
<tr>
<td>254</td>
<td>2.0</td>
<td>8.3</td>
<td>0.4</td>
<td>24°</td>
<td>1.3</td>
<td>7.9</td>
<td>4.0</td>
<td>28.6</td>
<td>45.7</td>
<td>0.05 0.28 0.14 2.06</td>
</tr>
<tr>
<td>274</td>
<td>2.0</td>
<td>6.5</td>
<td>0.4</td>
<td>23.5</td>
<td>19.25</td>
<td>96.8</td>
<td></td>
<td></td>
<td></td>
<td>0.07  (8.52)</td>
</tr>
<tr>
<td>275</td>
<td>2.2</td>
<td>7.7</td>
<td>22.9</td>
<td>24°</td>
<td>17.8</td>
<td>118.6</td>
<td></td>
<td></td>
<td></td>
<td>0.07  5.12</td>
</tr>
<tr>
<td>277</td>
<td>2.2</td>
<td>8.0</td>
<td>0.0</td>
<td>23°</td>
<td>36</td>
<td>142.6</td>
<td></td>
<td></td>
<td></td>
<td>0.05  0.14 0.11 2.93</td>
</tr>
<tr>
<td>278</td>
<td>2.2</td>
<td>6.3</td>
<td>2.3</td>
<td>23°</td>
<td>4.1</td>
<td>3.2</td>
<td></td>
<td>28.5</td>
<td>64.9</td>
<td>(0.04) 0.16 0.16 2.94</td>
</tr>
<tr>
<td>252</td>
<td>1.9</td>
<td>6.4</td>
<td>1.6</td>
<td>22°</td>
<td>6.3</td>
<td>7.4</td>
<td></td>
<td>45.4</td>
<td>49.8</td>
<td>(0.04) 4.2</td>
</tr>
<tr>
<td>281</td>
<td>2.0</td>
<td>6.2</td>
<td>5.1</td>
<td>22.3</td>
<td>0.9</td>
<td>4.97</td>
<td></td>
<td></td>
<td>37.1</td>
<td>121.3</td>
</tr>
<tr>
<td>282</td>
<td>2.0</td>
<td>6.2</td>
<td>5.1</td>
<td>22.3</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
<td>6.7</td>
<td>91.8</td>
</tr>
<tr>
<td>283</td>
<td>1.9</td>
<td>6.0</td>
<td>16.6</td>
<td>22.3</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
<td>37</td>
<td>108.5</td>
</tr>
<tr>
<td>284</td>
<td>2.05</td>
<td>6.4</td>
<td>14.8</td>
<td>22.5</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
<td>35.2</td>
<td>25.6</td>
</tr>
<tr>
<td>285</td>
<td>2.2</td>
<td>6.65</td>
<td>13.6</td>
<td>21.5</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
<td>32.4</td>
<td>175.5</td>
</tr>
<tr>
<td>287</td>
<td>1.8</td>
<td>5.95</td>
<td>12.6</td>
<td>22°</td>
<td>5.3</td>
<td>-</td>
<td></td>
<td>55</td>
<td>210.1</td>
<td></td>
</tr>
</tbody>
</table>

**Following Runs, Ketene, Ether pressures kept same, Air P varies. Time given 1½ Hrs.**

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Ketene (P cm)</th>
<th>Ether (P cm)</th>
<th>Air (P cm)</th>
<th>C.T.</th>
<th>MeOPri</th>
<th>BiPri</th>
<th>PriOBu₂</th>
<th>PriOBu₃</th>
<th>Acetone</th>
<th>Normalised to PriOBu₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>304</td>
<td>2.25</td>
<td>8.0</td>
<td>2.1</td>
<td>21°</td>
<td>1.1</td>
<td>3.6</td>
<td>3.76</td>
<td>42.1</td>
<td>43.6</td>
<td>(0.03) 0.08 0.09 1.03</td>
</tr>
<tr>
<td>305</td>
<td>2.2</td>
<td>8.0</td>
<td>7.05</td>
<td>22°</td>
<td>0.9</td>
<td>0.6</td>
<td>1.5</td>
<td>30.4</td>
<td>87.5</td>
<td>(0.03) 0.02 0.05 2.88</td>
</tr>
<tr>
<td>306</td>
<td>2.2</td>
<td>8.0</td>
<td>13.1</td>
<td>22°</td>
<td>-</td>
<td>2.6</td>
<td>v.small</td>
<td>24.6</td>
<td>-</td>
<td>- 0.11 v.small</td>
</tr>
<tr>
<td>307</td>
<td>2.2</td>
<td>8.0</td>
<td>16.6</td>
<td>23.5</td>
<td>-</td>
<td>4.4</td>
<td></td>
<td>23</td>
<td>144.6</td>
<td>- 0.19 v.small</td>
</tr>
<tr>
<td>308</td>
<td>2.25</td>
<td>8.0</td>
<td>2.25</td>
<td>23°</td>
<td>1.3</td>
<td>10.8</td>
<td>4.0</td>
<td>31.6</td>
<td>62.7</td>
<td>(0.04) 0.34 0.13 1.98</td>
</tr>
<tr>
<td>309</td>
<td>2.0</td>
<td>8.0</td>
<td>-</td>
<td>24°</td>
<td>1.75</td>
<td>13.1</td>
<td>5.5</td>
<td>24.3</td>
<td>37.1</td>
<td>0.07  0.54 0.23 1.52</td>
</tr>
</tbody>
</table>

**Average:** 0.06 varies 0.12 varies

**Molar Ratio:** 0.09 - 0.12 -
## Table 5.8

**EFFECT OF CARBON DIOXIDE**

**Irradiation:** Ketene + Diis Ether at 15-17°C

**Column:** Celite (DNF) Single

**N₂ flow:** 11 c.c.s/min.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Ketene P cm</th>
<th>Ether P cm</th>
<th>C.T.</th>
<th>Duration of Run</th>
<th>CO₂ P cm</th>
<th>PEAK AREAS</th>
<th>Normalized to Pr⁺OBu⁸</th>
<th>Molar Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>MeOPr⁺</td>
<td>BiPr⁺</td>
<td>Pr⁺OBu⁸</td>
</tr>
<tr>
<td>265</td>
<td></td>
<td></td>
<td>24°C</td>
<td></td>
<td>-</td>
<td>32.1</td>
<td>36.8</td>
<td>112.5</td>
</tr>
<tr>
<td>267</td>
<td>1.7</td>
<td>7.2</td>
<td>23.3°C</td>
<td>2 - 50</td>
<td>37.5</td>
<td>-</td>
<td>33.5</td>
<td>106.3</td>
</tr>
<tr>
<td>270</td>
<td>1.0</td>
<td>7.1</td>
<td>23.3°C</td>
<td>2 - 50</td>
<td>36.4</td>
<td>8.2</td>
<td>41</td>
<td>139.1</td>
</tr>
<tr>
<td>272</td>
<td>1.2</td>
<td>6.3</td>
<td>21.3°C</td>
<td></td>
<td>36.4</td>
<td>8.2</td>
<td>41</td>
<td>139.1</td>
</tr>
</tbody>
</table>

**Average:**

<table>
<thead>
<tr>
<th>MeOPr⁺</th>
<th>BiPr⁺</th>
<th>Pr⁺OBu⁸</th>
<th>Acetone</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.31</td>
<td>0.25</td>
<td>0.32</td>
<td>0.40</td>
</tr>
</tbody>
</table>

**Average Molar Ratio:**

| 0.08 | 0.32 | 0.40 |
### Table 5.9.1.

**EFFECT OF OXYGEN**  
**THE LOWER HYDROCARBONS**

Irradiation: Ketene + PriOPr at 132°C  
Column: Celite(S) + Act. Alumina (5 ft)(20-40 mesh)  
N₂ flow: 9 c.c.s/mt.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Ether Pcm</th>
<th>Ketene Pcm</th>
<th>Air Pcm</th>
<th>C.T.</th>
<th>PEAK AREAS</th>
<th>Normalized to Acetone</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Propylene</td>
<td>Isobutane</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>297</td>
<td>4.8</td>
<td>1.4</td>
<td>-</td>
<td>24.6</td>
<td>3.26</td>
<td>7.1</td>
</tr>
<tr>
<td>302</td>
<td>6.7</td>
<td>1.8</td>
<td>-</td>
<td>23.3</td>
<td>9.20</td>
<td>10.0</td>
</tr>
<tr>
<td>298</td>
<td>7.2</td>
<td>1.6</td>
<td>3.0</td>
<td>25.5</td>
<td>mixed up</td>
<td>1.8</td>
</tr>
<tr>
<td>299</td>
<td>6.7</td>
<td>1.3</td>
<td>2.8</td>
<td>24.5</td>
<td>2.4</td>
<td>3.3</td>
</tr>
<tr>
<td>300</td>
<td>7.5</td>
<td>1.9</td>
<td>2.7</td>
<td>24.3</td>
<td>3.0</td>
<td>3.9</td>
</tr>
<tr>
<td>301</td>
<td>5.65</td>
<td>1.85</td>
<td>2.2</td>
<td>24</td>
<td>1.96</td>
<td>4.67</td>
</tr>
</tbody>
</table>

### Table 5.9.2.

Irradiation: Ketene + PriOPr at 100°C  
N₂ flow: 17 c.c.s/mt. basis. for both cases.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Ether Pcm</th>
<th>Ketene Pcm</th>
<th>°C</th>
<th>Normalized to Acetone</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Ethane Propene Propylene Iso-butane</td>
</tr>
<tr>
<td>185</td>
<td>10.2</td>
<td>1.4</td>
<td>-</td>
<td>-                     0.06 0.13 0.24</td>
</tr>
<tr>
<td>188</td>
<td>7.5</td>
<td>1.5</td>
<td>43</td>
<td>0.03 0.08 0.2 0.23</td>
</tr>
<tr>
<td>189</td>
<td>9.9</td>
<td>1.2</td>
<td>43</td>
<td>0.02 0.05 (0.09) 0.14</td>
</tr>
<tr>
<td>190</td>
<td>8.0</td>
<td>2.8</td>
<td></td>
<td>0.01 0.05 0.11 0.20</td>
</tr>
<tr>
<td>191</td>
<td>6.8</td>
<td>2.0</td>
<td></td>
<td>0.02 0.06 0.15 0.22</td>
</tr>
<tr>
<td>Average:</td>
<td></td>
<td></td>
<td></td>
<td>0.02 0.06 0.15 0.22</td>
</tr>
<tr>
<td>Molar ratio:</td>
<td>0.19</td>
<td>0.19</td>
<td>0.47</td>
<td>0.27</td>
</tr>
</tbody>
</table>
FIG 11

- \( R\text{CH}_2\text{COCH}_3 / R'\text{OBu}^{\text{sec.}} \)
- \( R\text{BiR}^i / R'\text{OBu}^{\text{sec.}} \times 4 \)

Temperature in °C: 0, 50, 100, 150, 190
FIG 12
(duplicate)

\[ (b) \quad \text{ACETONE/Pr}^{i}\text{OBu}^{\text{sec}} \]

\[ (a) \quad \text{Pr}^{t}\text{OBu}/\text{Pr}^{i}\text{OBu}^{\text{sec}} \]
FIG 12

(a) ProBu/ProBu₂es
(b) ACETONE/ProBu₂es

- (b) 3.0 × 10⁻³ T (°K)
- (a) 3.5
6.1. DISCUSSION

Methylene generated photochemically reacts with ethers to give at least three major types of reaction. These are:

(1) Insertion Reaction in which CH$_2$ enters into a C-H bond.

(2) Displacement Reaction in which CH$_2$ gives rise to a methyl alkyl ether and displaces an olefin, e.g.

$$\text{C}_2\text{H}_5\text{OC}_3\text{H}_7 + \text{CH}_2 \rightarrow \text{CH}_3\text{OC}_3\text{H}_7 + \text{C}_2\text{H}_4$$

$$\text{C}_2\text{H}_5\text{CC}_3\text{H}_7 + \text{CH}_2 \rightarrow \text{C}_2\text{H}_5\text{CC}_3\text{H}_7 + \text{C}_2\text{H}_6$$

(3) Abstraction Reaction in which CH$_2$ behaves like a monoradical and abstracts hydrogen from the ether to give another radical which may break down into an aldehyde or ketone and an alkyl radical. When oxygen is added to the system peroxy radicals are formed. These can initiate short chains particularly above 100°C. Reactions (1) and (2) are relatively unaffected by added oxygen.

6.2. THE INSERTION REACTION

In the reaction of methylene with ethers, insertion into C-H bonds is the major reaction. These insertions have been found to show clear discrimination: insertion into secondary bond is faster than into tertiary and into tertiary slightly faster than into a C-H bond. The products of insertion reaction with ethers so far studied are:

(1) $^{13}$CH$_2 + \text{CH}_3\text{OC}_2\text{H}_5 \xrightleftharpoons{k_1} \text{CH}_3\text{OC}_2\text{H}_5$

(2) $^{13}$CH$_2 + \text{C}_2\text{H}_5\text{OC}_2\text{H}_5 \xrightleftharpoons{k_2} \text{C}_2\text{H}_5\text{Ciso-C}_3\text{H}_7$

(3) $^{13}$" + " $\xrightleftharpoons{k_3} \text{C}_2\text{H}_5\text{CnC}_3\text{H}_7$

(4) $^{13}$CH$_2 + \text{C}_2\text{H}_5\text{OC}_3\text{H}_7 \xrightleftharpoons{k_4} \text{C}_2\text{H}_5\text{Ciso-C}_4\text{H}_9$
The experimental data can best be summarised by Table 6.1. The bond reactivity, as stated earlier, has been calculated after allowing for the difference in the number of bonds concerned. For MeO\textsubscript{2}Me, the value of 1.72 for bond reactivity based on unity for the \( \delta \) bond in EtOEt indicates marked selectivity of attack for \( \delta \) of dimethyl ether. In EtOEt, the reactivity for \( \delta \) at 100°C is 2.79 based on 1.00 for \( \delta \), so that \( \delta \) bond is attacked 2.79 times as fast as the \( \delta \) bond. At 20°C, they are attacked 2.63 times as fast as primary. The rate of abstraction of \( \delta \) H atoms relative to insertion at a \( \delta \) bond was found to be 0.32. The cumulative rate of attack at 20°C becomes 2.95. At 100°C, the H-abstraction rate is \( \approx 1.0 \) although individual runs show much variation. The cumulative rate of attack at 100°C is thus about 3.8 times greater than on the primary. The results are therefore consistent with those of Doering et al.\textsuperscript{29} and of Frey and Kistiaikowsky\textsuperscript{22}.

The bond reactivity for EtOPr\textsuperscript{3} based on unity for the primary of ethyl group, again proves the discriminate attack of methylene. All secondary bonds here are attacked faster than primary of ethyl, the \( \delta \) C-H of ethyl itself being attacked 1.83 times and is higher than the secondary \( \alpha \) C-H and \( \beta \) C-H bonds which are 1.74 and 1.29 respectively. The descending order of reactivity of C-H bonds in propyl group is remarkable: \( \alpha > \beta > \gamma \) (Fig. section 4.1.1.). The higher rate of attack on \( \alpha \) secondary bond is possibly due to closer
proximity to oxygen of ether. Similarly, the preference of attack on \( C-H \) of MeOME over those of EtOEt compared to those of propyl group in EtOPr\(^n\) are 1.72, 1.00, 0.92, again indicating the electrophilic effect of oxygen being operative; the farther the bond from oxygen the lower is the rate of insertion.

Table 6.1 also shows the small and random effect of temperature on the relative insertion rates. The effects are about within experimental error and show that the activation energy difference between different insertion reactions is at most a few hundred cals. The results agree with those of other workers\(^{32}\) who have shown that the activation energy for insertion of \( CH_2 \) into primary bond of alkanes is only very slightly different from that for insertion into \( \beta \) and \( \gamma \) bonds. However, the relative A factors cancel out this difference so that relative rate of attack was approximately, but not exactly, statistical. These results obtained in gas phase contrasted with those of Doering et al.\(^{17}\) who found that in the liquid phase the insertion reaction with both ethers and hydrocarbons was indiscriminate. The present results again confirm the difference between the two phases. The very low activation energy differences suggest that the absolute values are very low. In this respect the insertion reaction differs from the abstraction which have much high temperature coefficient activation energies and A factors.

6.3. **DISPLACEMENT REACTION**

Methylene has been found to displace an olefin from an ether and yields a methyl alkyl ether. The discovery of this novel reaction has been fully established by detailed studies into symmetrical and asymmetrical ethers under varying conditions of temperature. The following reactions have been noted:
# TABLE 6.1.

**Insertion and Displacement of Methylene**

<table>
<thead>
<tr>
<th>Ether</th>
<th>Bond Attacked and No. of identical bonds</th>
<th>Product formed X</th>
<th>Standard Product S</th>
<th>Amount X/S</th>
<th>Bond Reactivity</th>
<th>Amount X/S</th>
<th>Bond Reactivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>MeOMe</td>
<td>Pri in MeOMe 6</td>
<td>EtOMe</td>
<td>EtOPr (6)</td>
<td>1.72</td>
<td>1.72</td>
<td></td>
<td></td>
</tr>
<tr>
<td>EtOEt</td>
<td>Pri 6</td>
<td>EtOPr</td>
<td>EtOPr (6)</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td></td>
<td>Sec 4</td>
<td>EtOPri</td>
<td>EtOPri</td>
<td>1.86</td>
<td>2.79</td>
<td>1.75</td>
<td>2.63</td>
</tr>
<tr>
<td></td>
<td>Et-0 2</td>
<td>MeOEt</td>
<td>EtOPri</td>
<td>0.38</td>
<td>1.14</td>
<td>0.46</td>
<td>1.38</td>
</tr>
<tr>
<td>EtOPr</td>
<td>Pri in Pr 3</td>
<td>EtOBu</td>
<td>PrOP (3)</td>
<td>0.92</td>
<td>0.92</td>
<td>0.38</td>
<td>0.87</td>
</tr>
<tr>
<td></td>
<td>Sec in Pr 2</td>
<td>EtOBu</td>
<td>PrOP (3)</td>
<td>1.29</td>
<td>2.3</td>
<td>3.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>sec in Pr 2</td>
<td>EtOBu</td>
<td>PrOP (3)</td>
<td>1.16</td>
<td>1.74</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Pr-0 1</td>
<td>MeOEt</td>
<td>PrOP (3)</td>
<td></td>
<td>0.24</td>
<td>0.72</td>
<td>0.60</td>
</tr>
<tr>
<td></td>
<td>Pri in Et 3</td>
<td>PrOPr</td>
<td>PrOPr (3)</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td></td>
<td>Sec in Et 2</td>
<td>PrOPr</td>
<td>PrOPr (3)</td>
<td>1.22</td>
<td>1.83</td>
<td>1.32</td>
<td>1.98</td>
</tr>
<tr>
<td></td>
<td>Et-0 1</td>
<td>MeOPr</td>
<td>PrOPr (3)</td>
<td>0.37</td>
<td>1.11</td>
<td>0.30</td>
<td>0.90</td>
</tr>
<tr>
<td>PrOPri</td>
<td>Pri C-H 12</td>
<td>PrOBu</td>
<td>PrOBu (12)</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td></td>
<td>ter 2</td>
<td>PrOBu</td>
<td>PrOBu (12)</td>
<td>0.17</td>
<td>1.02</td>
<td>0.25</td>
<td>1.50</td>
</tr>
<tr>
<td></td>
<td>Pri-0 2</td>
<td>MeOPr</td>
<td>PrOPr (3)</td>
<td>0.09</td>
<td>0.54</td>
<td>0.13</td>
<td>0.78</td>
</tr>
</tbody>
</table>
From Table 6.1, we have the following results for displacement reactions:

<table>
<thead>
<tr>
<th>Ether</th>
<th>Bond attacked</th>
<th>100°C Bond Reactivity relative to 1 C-H</th>
<th>20°C Bond Reactivity relative to 1 C-H</th>
</tr>
</thead>
<tbody>
<tr>
<td>EtOEt</td>
<td>Et-0</td>
<td>1.14</td>
<td>1.38</td>
</tr>
<tr>
<td>EtOPr^1</td>
<td>Et-0</td>
<td>1.11</td>
<td>0.90</td>
</tr>
<tr>
<td>Pr^1OPr^1</td>
<td>Pr^1-0</td>
<td>0.54</td>
<td>0.78</td>
</tr>
</tbody>
</table>

The bond reactivity for Et-0 in the two ethers above is 1.14, 1.11, which are within experimental limits of accuracy the same at 100°C. The lower value at both temperatures for Pr-0 and Pr^1-0 indicates steric hindrance, being more for a branched isopropyl group compared to n-propyl group.

It is likely that the ether split goes through a cyclic transition state where methylene attacks the C-O bond of the ether followed by a shift of an adjacent hydrogen atom. Thus for example, ethyl group of EtOEt breaks down to form ethylene, while propyl and isopropyl groups in the corresponding ethers yield propylene in the same manner. The break of C-alkyl bond was first noticed in the case of attacking proton of Lewis acid, strong bases or ether radical; possibly methylene with its two vacant orbitals attacks the oxygen atom of ether possessing two unpaired electrons where the latter acts as a Lewis base (which by definition is an electron donor) thus forming a coordinate bond. Here the two unpaired electrons of oxygen may occupy the vacant p orbital of CH₂.
thereby a positive charge on oxygen atom will be induced. Simultaneously, any of the three SP^2 orbitals will interact with the P orbital of CH₂. In other words, owing to the presence of its unpaired electrons, methylene acts as a strong base and therefore can abstract the adjacent hydrogen atom as a proton. A transition state as follows is possible:

\[
C_2H_5OCH_2CH_3 + CH_2 \rightarrow C_2H_5CH = CH_2 + C_2H_5OC\overset{\text{H}}{\text{O}} = CH_2
\]

Though Franzen believes that \(\alpha\) hydrogen shift takes place, it is not certain that \(\beta\) hydrogen does not. For isopropyl ether a similar shift of hydrogen from the \(\alpha\) carbon takes place, the tertiary hydrogen shift gives rise to isopropyldiene biradical which may isomerise to propylene. Thus the split of C-O bond and hydrogen shift takes place simultaneously without involving a free radical since increase in oxygen pressure did not change the rate ratios for the methyl alkyl ether by giving rise to oxygenated products. Due to the electron deficiency of CH₂, the expected preference of attack on the C-Cl bond of isobutyl chloride compared to C-H has been shown.

The reaction of carbethoxy carbene with di-n-butyl ether has been reported to give alkoxyacetic acid and but-1-ene. Now CH₂OCET is more electropositive than CH₂; thus a relatively higher positive charge is introduced on oxygen atom which would give an easier split of a proton from the neighbouring carbon. In all these cases a cyclic transition state is involved, indicating
a similarity to the methylene attack. It is also probable that thioethers react in the same way during methylation when C-S bond breaks.

Fig.7 shows a plot of the molar ratio MeOEt/EtOPr® against air pressure. The curve shows a rise up to 15 cm but is not genuine rise, being due to the fall in the absolute amount of EtOPr® with increase in air pressure (Fig.4A). Indeed such a rise was not found for MeOPri/Pr®OBu® where the absolute amount of Pr®OBu®, unlike EtOPr®, did not fall with the increase of air added to the system. Thus the direct reaction of methylene to give displacement of olefin from ether is proved by the absence of the effect of oxygen.

As with the insertion reactions the displacement reactions show very small temperature coefficients. They occur at comparable speeds and one may therefore deduce that their activation energies are low and that the transition states are similar both being cyclic and involving the subsequent transfer of an H atom from a neighbouring C atom.

6.4. ABSTRACTION REACTIONS

Methylene has been found to give H-abstraction, a property normally associated with monoradicals. It abstracts 2 and 3 hydrogen in ethers as shown from the products produced but it is not certain whether primary hydrogen is abstracted. Table 6.4 lists the bond reactivity by abstraction relative to the insertion into the primary C-H bond.
**TABLE 6.4**

<table>
<thead>
<tr>
<th>Ether</th>
<th>Bond attacked</th>
<th>Product formed</th>
<th>Standard product</th>
<th>Amount X/S</th>
<th>Bond Reactivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>EtOEt</td>
<td>sec C-H</td>
<td>CH₃CHO</td>
<td>EtOPr</td>
<td>0.92</td>
<td>1.38</td>
</tr>
<tr>
<td>EtOPr</td>
<td>sec α, β in Pr</td>
<td>C₂H₅CHO</td>
<td>Pr⁰OPr</td>
<td>varies</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>sec C-H in Et</td>
<td>CH₃CHO</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>Pr³OPr⁴</td>
<td>ter C-H</td>
<td>CH₃COCH₃</td>
<td>Pr³CEu</td>
<td>1.19</td>
<td>7.14</td>
</tr>
</tbody>
</table>

The values for abstraction of sec hydrogen of EtOPr at room temperature have been found but at 100°C the variation is large (Table 4.1.1, 4.1.2) and therefore omitted from the table above. It is seen, however, that abstraction of tertiary is between 2 and 5 times as fast as abstraction secondary H atom. To obtain the total reactivity of C-H bond, therefore, the values for abstraction may be added to the insertion values. These were for 2 2.79 and for tertiary 1.02 at 100°C. Such a consideration has often been ignored by previous workers. We then have the order of total bond reactivity as tertiary > secondary > primary and follows the sequence of bond dissociation energies given by Cottrell:

<table>
<thead>
<tr>
<th>Bond attacked</th>
<th>Tertiary</th>
<th>Secondary</th>
<th>Primary</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Bond Reactivity</td>
<td>8.16</td>
<td>4.17</td>
<td>1.0</td>
</tr>
<tr>
<td>Bond Strength</td>
<td>89</td>
<td>94</td>
<td>96</td>
</tr>
</tbody>
</table>

6.4.1. **POSSIBLE MECHANISM**

The direct reaction of methylene by insertion has been proved by the absence of oxygen effect. The abstraction reaction may itself be independent of oxygen although the products aldehyde, ketones increased owing to the direct attack of alkyl radicals by oxygen. Basically these are elementary reactions
although the mode of attack of CH₂ by insertion and abstraction may involve different intermediates:

\[
\begin{align*}
\text{Complex for insertion} & \quad \text{Complex for abstraction} \\
\text{O} - \text{C} - \text{O} - \text{H} & \quad \text{O} - \text{C} - \text{H} - \text{C} - \text{O} - \text{H} \\
\text{H} & \quad \text{H}
\end{align*}
\]

The product of abstraction reaction from ethers were found to increase greatly with the rise in temperature. Obviously at 100°C and above, the methyl radicals generated by H-abstraction and other monoradicals contribute to this increase. Thus the molar rate of abstraction/bond for tertiary hydrogen based on unity for insertion into 0 C-H in Pr₁OPr₁ for example, is:

\[
\begin{align*}
\text{CH₃} & \quad \text{O} - \text{C} - \text{H} - \text{CH₃} \\
\text{O} - \text{C} - \text{H} & \quad \text{CH₃}
\end{align*}
\]

\[
\begin{align*}
1.3 & \text{ at } 16°C \\
4.3 & \text{ at } 68.7°C \\
7.1 & \text{ at } 100°C \\
11.1 & \text{ at } 132°C \\
19.8 & \text{ at } 190°C
\end{align*}
\]

The aldehydes formed by H-abstraction in EtOEt and EtOPr₃ increase manifoldly with the increase in temperature; acetone yields increased also with the rise in temperature and so did bi-isopropyl (Fig.11). Acetaldehyde seems to be formed by the following mechanism:

\[
\begin{align*}
\text{CH₂} + \text{C₂H₅OC₂H₅} & \rightarrow \text{CH₃} + \text{CH₃CHOOC₂H₅} \quad \ldots \ldots (1) \\
\text{CH₃CHOOC₂H₅} & \rightarrow \text{CH₃CHO} + \text{C₂H₅} \quad \ldots \ldots (2) \\
2 \cdot \text{C₂H₅} & \rightarrow \text{C₄H₁₀} \quad \ldots \ldots \ldots (3)
\end{align*}
\]

In EtOPr₃, there are two groups from which 2 hydrogen can abstract and a corresponding aldehyde is formed. Acetaldehyde and propionaldehyde are formed as follows:
The monoradicals thus produced may give H-abstraction above 100°C or dimerise, cross combine, to yield the lower hydrocarbons found as minor products.

The various steps involved in the abstraction of tertiary hydrogen are shown in section 5.4.1. The isopropyl ether radical breaks up into Pr\textsuperscript{1} radical and acetone. Such a split has been postulated\textsuperscript{91} by the H-abstraction given by methyl radical. Thus a similar monoradical reaction is given by methylene. After this research was completed, a note has been published by Frey\textsuperscript{96} where parallel abstraction of tertiary H from isobutane has been postulated. Though Frey has not been able to isolate octane, he found large quantities of isobutene produced by disproportionation of isobutyl radical.

In order to determine the extent of H\textsuperscript{9} H-abstraction quantitatively, a detailed study on di-isopropyl ether has shown that this is a considerably fast reaction even at room temperature. Increase in temperature yields manifold quantities of acetone as a result of H-abstraction because H-abstraction by monoradicals augments the rate. The H-abstraction from H\textsuperscript{2} hydrogen in Et\textsubscript{2}Et and Et\textsubscript{2}Pr\textsuperscript{11} is around 0.11. It is about eight times faster with tertiary H in Pr\textsuperscript{1}OPr\textsuperscript{1} at room temperature. At 190°C, for example, a fifteen-fold increase has been found.

The apparent activation energy difference found by plotting the relative rate of formation of methylene was 3.8 kcal. The data at 20° and 100°C for Abstraction of the secondary H-atom from Et\textsubscript{2}Et yield a similar
activation energy difference. They react with higher activation energies than the insertion reaction but with comparable rate have much higher $A$ factors, by a factor of 100 or more. This casts some doubt on the conclusion of Kistiakowsky that methylene reacts in about 100 collisions or less.

6.4.1. THE LOWER HYDROCARBONS

The $H$-abstraction reaction by methylene gives rise to methyl radicals\(^{105}\) which can dimerise to yield ethane step (4) below. Frey and Kistiakowsky\(^{106}\) have postulated this reaction in the attack of $\text{CH}_2$ on alkanes where the relative yield of ethane was the same whether propane or butane was used. All methyl radicals do not dimerise as shown in the discussion (6.3.3) but also disappear by cross combination with other monoradicals. At $100^\circ\text{C}$, the molar rate ratio for ethane is 0.02 only. The other reactions are:

\[
\begin{align*}
(\text{iso-C}_2\text{H}_7)_2 \text{O} + \text{CH}_2 & \rightarrow (\text{CH}_3)_2 \text{CO} + .\text{CH}_3 + .\text{CH}(.\text{CH}_3)_2 \cdots \quad (1) \\
\text{CH}_3 + \text{CH}(.\text{CH}_3)_2 & \rightarrow \text{CH}_3\text{CH}(.\text{CH}_3)_2 \cdots \cdots \cdots \quad (2) \\
2 .\text{CH}(.\text{CH}_3)_2 & \rightarrow 2,3, \text{ dimethyl Butane} \cdots \cdots \cdots \quad (3) \\
\text{CH}_3 + \text{CH}_3 & \rightarrow \text{C}_2\text{H}_6 \cdots \cdots \cdots \cdots \quad (4) \\
2 \text{CH}(.\text{CH}_3)_2 & \rightarrow \text{C}_3\text{H}_6 + \text{C}_3\text{H}_8 \cdots \cdots \cdots \cdots \quad (5)
\end{align*}
\]

All the products predicted by steps (1) to (5) have been found and measured quantitatively, which led to the conclusion that the mechanism of acetone formation is correct. The lower hydrocarbons arising from the reaction of isopropyl and methyl radicals (step 1) have been found to be equimolar to acetone. Thus a total of 1.07 (section 5.3.1) was obtained after deducting the amount of propylene formed from displacement reaction, and proves the authenticity of the above mechanism.
The propane and propylene (5) are formed by disproportionation. To test this point further, oxygen was added to the system. Small additions of air up to 3 cm pressure reduced the molar ratio of propylene as well as isobutane (Table 5.9.1) which also shows that the Pr\(^{\dagger}\) radical is being oxidised (6.5.2). The reduction in the rate of step (5) is in conformity with the observation of Frey\(^{96}\) where isobutane was not formed from Bu\(^{\dagger}\) radicals in the presence of oxygen.

6.5. EFFECT OF ADDED GASES

The effect of inert gas like CO\(_2\), though not truly inert\(^{49}\), and propane, oxygen on the relative rates of formation of the products of Insertion, Displacement, and Abstraction have been given in the preceding chapters. Here we will discuss the major features of the part played by these gases.

6.5.1. INERT GAS, CARBON DIOXIDE

The role of CO\(_2\) in the reaction of methylene with Pr\(^{\dagger}\)OPr\(^{\dagger}\) was followed in some detail at 16\(^{\circ}\)C and 132\(^{\circ}\)C. At 16\(^{\circ}\)C, the relative rate of insertion product, Pr\(^{\dagger}\)OBu\(^{\dagger}\), showed a small increase from 0.25 to 0.32 but at 132\(^{\circ}\)C there was no change from the value.

The displacement reaction showed a decrease for relative amounts of MeOPr\(^{\dagger}\) from 0.13 to 0.09 on the addition of 36.4 cm CO\(_2\) at room temperature. Similarly at 132\(^{\circ}\)C, the value showed a small fall from 0.08 to 0.06. The product of abstraction, acetaldehyde, increased at room temperature but at 132\(^{\circ}\)C the variation was large (Table 5.6) though the values are always lower than \(1.86\) as obtained in the absence of added gas. Similarly, the relative yield of acetone also showed a rise from 0.22 to 0.40 at 16\(^{\circ}\)C but at 132\(^{\circ}\)C the values are lowered due to the presence of CO\(_2\). The variation (Table 5.6) being large, an average cannot be taken. This indicated that CO\(_2\) is reactive at higher temperatures.
for displacement process but not for the insertion. In diethyl ether, the value \( \text{EtOPr}^i / \text{EtOPr}^n \) showed a fall when \( \text{CO}_2 \) was added (Table 3.2.4); a value of 1.82 in the presence of propane became 1.54. Addition of small amounts of oxygen (air 1 cm or so) to the same system gave a value 1.90 in place of 1.52.

6.5.2. **REACTIVE GASES. \( \text{O}_2, \text{C}_3\text{H}_8 \)**

The absolute amount of products of insertion, \( \text{EtOPr}^i \) and \( \text{EtOPr}^n \) shows a decline in the initial region of air pressure say 10 cm, but remains unaffected by further increase. The ratio \( \text{EtOPr}^i / \text{EtOPr}^n \) remains unaffected from 1 - 45 cm air, below 1 cm air showed a fall (Fig.8). The addition of larger concentrations of propane to the system containing keten and EtOEt did not show any change in the value of \( \text{EtOPr}^i / \text{EtOPr}^n \). Methylene inserts itself directly into the C-H bonds. The absolute amount of product of displacement, MeOEt, remains unaffected by the addition of oxygen (Fig.9). With diisopropyl ether, the insertion products show a decrease with the increase of oxygen (air 7-8 cm). At higher air pressure it becomes too small to be measured on a chromatogram. This fall is associated with the increase of acetone formation, but not of biisopropyl; isopropyl radicals are consumed to yield acetone:

\[
\text{CH}_3\text{CHCH}_3 + \text{O}_2 \rightarrow (\text{CH}_3)_2 \text{CHO} \quad \ldots \ldots \ldots \ldots\ldots \ldots (1)
\]

\[
(\text{CH}_3)_2 \text{C-H} \rightarrow (\text{CH}_3)_2 \text{CO} + \text{OH} \quad \ldots \ldots \ldots \ldots (2)
\]

At 132°C, for example, the molar ratio acetone/biisopropyl = 11.1 (Table 5) whereas, in the presence of oxygen (about 2 cm), it was on molar basis = 40. Such an increase in the relative amounts is understandable in view of the step above.

The isopropyl peroxy radical formed in step (1) would also give rise to acetaldehyde and methoxyl radical. We can therefore account for the increase in the formation of aldehydes from EtOEt and EtOPr\(^n\) because reactions of
propyl-peroxy radicals are exothermic to the extent shown below:

\[(a) \quad n-C_3H_7OO = C_2H_5CHO + OH \quad \Delta H = -40 \text{ kcal}\]

\[(b) \quad \text{iso-}C_3H_7OO = CH_3CHO + OCH_3 \quad \Delta H = -40 \text{ kcal} \]

Step (b) may be followed by (c)

\[(c) \quad CH_3O + O_2 = CH_2=O + HO_2 \quad \Delta H = -23 \text{ kcal}\]

The aldehydes formed by H-abstraction in EtOEt, and EtOPr, increase with addition of oxygen to the system. The absolute amount of acetaldehyde increases with the addition of air (Fig.6). The primary abstraction process gives ether monoradical which breaks up to give ethyl radical in case of EtOEt, thus

\[\cdot C_2H_5 + O_2 \rightarrow C_2H_5OO \rightarrow CH_3CHO + \cdot OH \quad \ldots \ldots \ldots \ldots \ldots \ldots (6)\]

\[\cdot C_3H_7 + O_2 \rightarrow C_3H_7OO \rightarrow C_2H_5CHO + \cdot OH \quad \ldots \ldots \ldots \ldots \ldots \ldots (7)\]

In the absence of air the molar rate ratio for acetaldehyde at 100°C was 0.92 but rose to 18.0 on the addition of air up to 31.6 cm. Clearly the ethyl radicals are oxidised rapidly at such pressures before they have a chance to react between themselves, with other monoradicals etc. The variation of acetaldehyde and ethyl acetate follows the same pattern (compare Fig.10,3) - a sharp rise up to 4 cm is indicated. The point where the peak starts descending corresponds to the maximum consumption of oxygen possible by the available free radicals. This has been shown as follows: The concentration of keten, ether and air being fixed (2 cm), the time of irradiation was varied. The 2 cm air corresponding to the rising region of the peak showed no increase in the absolute yield of ethyl acetate, proving the complete consumption of oxygen by the ether monoradical.

6.5.2.1. THE MECHANISM OF ESTER FORMATION

The formation of esters in the reaction of methylene with diethyl
ether was studied at some length to elucidate the mechanism of oxidation of ether radical released by H-abstraction. It was found that when acetone was used, as source of methyl radicals, in the presence of oxygen and ether (Run 411), ethyl acetate was formed to a small extent. It seemed, therefore, that here, whether methyl or methylene be involved, they are showing a monoradical property. The concentration of methyl radical, in our system (keten + EtOEt) was too small to account for the large amount of ethyl acetate and ethyl formate; the latter was almost 2.5 times the former. Even at room temperature (air = 44.0 cm), the molar rate ratio for ethyl acetate rises to twenty times its value at low concentration (0.3 cm air) of air. It seemed, therefore, that the following plausible scheme would fit into the kinetics of reaction adequately:

**CHART 1**

\[
\begin{align*}
\text{CH}_3\text{CH}_2\text{CO}_2\text{H}_5 + \text{CH}_2 & \rightarrow \text{CH}_3\text{CHOCO}_2\text{H}_5 + \cdot\text{CH}_3 \quad (1) \\
+ \cdot\text{CH}_3 & \rightarrow \cdot\text{CH}_2 + \text{CH}_4 \quad (2) \\
\text{CH}_3\text{CHOCO}_2\text{H}_5 & \rightarrow \text{CH}_3\text{CHO} + \cdot\text{C}_2\text{H}_5 \quad (3) \\
\cdot\text{C}_2\text{H}_5 + \text{O}_2 & \rightarrow \text{CH}_3\text{CHO} + .\text{OH} \quad (4) \\
\text{RO}_2 + .\text{C}_2\text{H}_5\text{CO}_2\text{H}_5 & \rightarrow \text{CH}_3\text{CHOCO}_2\text{H}_5 \quad (5) \\
\text{CH}_3\text{CHOCO}_2\text{H}_5 + \text{O}_2 & \rightarrow \text{CH}_3\text{CHOCO}_2\text{H}_5 \quad (6) \\
\end{align*}
\]

In general, \( R. + \text{O}_2 \rightarrow \text{ROO.} \) \( \quad (7) \)

\[ \text{ROO} + \text{RH} \rightarrow \text{ROOH} + R. \quad \text{Propagation} \]

\[ \text{R.} + \text{R} \rightarrow \text{Inactive products} \]

\[ \text{R.} + \text{ROO.} \rightarrow \]

\[ \text{ROO.} + \text{ROO.} \rightarrow \]
In addition to the above, there are, of course, various possibilities.

\[
\begin{align*}
\text{CHART 2} \\
\text{C}^*\text{H}_2 + \text{O}_2 & \rightarrow \text{CH}_2\text{CO} \quad \ldots \ldots \quad (9) \\
\text{C}^*\text{H}_3 + \text{O}_2 & \rightarrow \text{CH}_3\text{O}_2 \quad \text{(Products)} \quad \ldots \ldots \quad (10) \\
\text{CH}_2 + \text{CH}_2\text{CO} & \rightarrow \text{C}_2\text{H}_4 + \text{CO} \quad \ldots \ldots \quad (11) \\
\text{C}^*\text{R} + \text{O}_2 & \rightarrow \text{RO}_2 \quad \ldots \ldots \quad (12)
\end{align*}
\]

The rate constant for step (10) has been estimated to be \(= 10^{-16}\) ml/molecule sec, and for (9) \(5 \times 10^{-4}\) ml/molecule sec, which is about 500 times greater. Also the activation energy for both the reactions is about 98-100 kcal/ mol while that for step (1) of about 15 kcal also shows how important steps (9) and (10) can be. The steric factors for (9) and (10) are also quite compatible; for the former it is estimated to be about \(10^{-3}\) and for the latter it is \(2 \times 10^{-4}\). The activation energy for reaction (6) is known to be zero so that reaction (1) is readily followed by (6) and there is no evidence that the insertion process may consist of radical combination process, \(\text{C}^*\text{H}_3 + \text{CH}_3\text{CHCC}_2\text{H}_5 \rightarrow \text{C}_3\text{H}_7\text{OCC}_2\text{H}_5\) because in the presence of oxygen, even in large amounts where ether radical would be consumed almost completely by (6), no significant change in relative amounts of EtOPr\(^i\)/EtOPr\(^n\) is shown.

\[ [\text{CH}_3] \] concentration in the system has been calculated and found to be approximately \(3.3 \times 10^{-13}\) mole cc\(^{-1}\). It having been established that methyl radicals (generated from acetone) also yield esters, the conclusion is that the initiation step (1) above is essentially an abstraction process where \(\text{CH}_2\) acts as a monoradical, like \(\text{CH}_3\) in step (2).

An approximate molar ratio of ethyl formate to ethyl acetate is 2.5 and there is no doubt a possibility that this may be due to difference in the rate of steps (6A) and (6B). The free radicals formed in the system may form
peroxy radicals as in step (7) shown as a general case. It is quite possible that some such monoradicals chin carriers are formed which give abstraction reaction too, as in step (5). Step (9) involves chain carriers like true radicals\textsuperscript{101}. The chain process is indicated in Chart 1 and accounts for the large yields of ester since this is preceded by abstraction reaction by several steps i.e. (1), (2), (5), (7), and (9). The chain terminating steps are shown in (8). It was shown in the experimental part that ethyl acetate arises from a complete consumption of oxygen required by the free radicals in the initial region of the curve.

The addition of oxygen to the system :CH\textsubscript{2} + EtOPr\textsuperscript{+} was investigated after it was clear from similar studies on EtOEt that esters are formed. Small traces of oxygen were tried to avoid complication in the isolation of already many products of reaction which showed overlap. Recent experiments carried out at 100\textsuperscript{o}C were Runs 470, 471, 472-476. Two new peaks appeared where 12 ft of celite (80-100) 20% squalane was used. The new peaks correspond to the two esters. The product analyses then became complicated owing to the additional peaks on the chromatogram. Thus peroxy radicals are formed, following H-abstraction, by the attack of oxygen on ether monoradical in three different positions, such as,

\[ \text{CH}_3\text{CHOC}_3\text{H}_7 + \text{O}_2 \rightarrow \text{CH}_2\text{CHOC}_3\text{H}_7 \quad \text{(5)} \]

or

\[ \text{C}_2\text{H}_5\text{OCCH}_2\text{CH}_3 + \text{O}_2 \rightarrow \text{CH}_2\text{OCCH}_2\text{CH}_3 \quad \text{(6)} \]

or

\[ \text{C}_2\text{H}_5\text{OCCH}_2\text{CH}_3 + \text{O}_2 \rightarrow \text{C}_2\text{H}_5\text{OCCH}_2\text{CH}_3 \quad \text{(7)} \]

and the esters formed from (5) and (6) are dependant on which hydrogen or group is abstracted by an oxygen atom. Step (5) could give propyl acetate and propyl formate; (6) could give ethyl propionate and ethyl formate;
(7) could give ethoxy acetone or ethoxy acetaldehyde. It was shown that at 100°C the addition of even large amounts of oxygen did not affect the insertion products. Less than 1 cm of air, on the other hand, reduces the discriminatory mode of attack. In agreement with Frey and Kistiakowsky\textsuperscript{22}, it may be inferred that methylene at the point of its creation carries extra vibrational energy which is spread out in a wide range. The more energized fraction giving rise to discriminatory attack is easily deactivated at relatively low pressures of inert gases, above which it has no effect on the rest of methylene biradicals. Fig. 8 shows $R(\text{EtOPr}^1/\text{EtOPr}^2)$ falls only in the region of 1 cm or so of air but remains steady after that. The effect of propane has been shown to be negligible on the above ratio. The obvious conclusion is that CH$_2$ attacks propane and ether with equal facility and "quenching" is not effective in this case. The effect of carbon dioxide (not a completely inert gas) is to lower the value of $R$ from 1.75 to 1.3 which increases to 1.61 on the addition of about 1 cm of air or so (Table 3.2.4) still remains to be explained.

The role of oxygen was last to be studied. The formation of hydroperoxides has been postulated in the present work as in the gas phase oxidation work. Whether the 2.5 times molar ratio for ethyl formate involves a common intermediate for the esters isolated needs further study using substituted ethers. Also, the reactions of peroxide radicals with hydrocarbons need further investigation. The shift of primary hydrogen as a proton can be easily shown by the production of MeOEt from displacement reaction with ethyl t-butyl ether. Thus methylene will give rise to acetylene and allene by the displacement reaction with methyl vinyl and methyl allyl ether respectively.
\[
\begin{align*}
\text{CH}_2 + \text{CH}_3\text{OCH} & = \text{CH}_2 \rightarrow \text{CH}_3\text{OCH}_3 + \text{CH} = \text{CH} \\
+ \text{CH}_3\text{OCH}_2\text{CH} & = \text{CH}_2 \rightarrow " + \text{CH}_2 = \text{C} = \text{CH}_2 \quad \text{(Allene)} \\
\text{or} \quad \text{CH}_3\text{C} & = \text{CH} \quad \text{(Propyne)}
\end{align*}
\]

It will be of great interest to know whether the \( \text{H} \)-abstraction of allylic or vinylic group followed by the oxygen attack will result in the formation of formaldehyde and carbon monoxide.

The hydrogen shift from benzene ring can be shown by work on methyl or ethyl phenyl ether. The following possibilities can again be predicted:

(a) \[
\begin{align*}
\text{O} & \rightarrow \text{C}_2\text{H}_5 + \text{CH}_2 \rightarrow \text{CH}_3\text{OC}_2\text{H}_5 + \text{iC}_6\text{H}_4
\end{align*}
\]

(b) \[
\begin{align*}
\text{CH}_2 & \rightarrow \text{O} \rightarrow \text{C}_2\text{H}_5
\end{align*}
\]

(c) \[
\begin{align*}
\text{MeOE} & \rightarrow \text{MeOEt} \rightarrow \text{MeOC}_2\text{H}_5
\end{align*}
\]

Thus MeOE is expected to arise from the hydrogen shift from benzene ring.

There are, of course, many possibilities like the insertion into C-O if 'ylid' mechanism were true although no insertion at C-O bond of tetrahydrofuran has been found. Similarly, much remains to explore into the novel displacement and abstraction reaction, in substituted hydrocarbons, amines and heterocyclics to see whether C-C, C-N bonds rupture. Thus we see that a large and fascinating field for study is thrown open.
BIBLIOGRAPHY

2 Duffey. ibid. 17 (1949), 840.
3 Skell and Woodworth, J.A.C.S. 81 (1959), 3383.
   b " Nature Vol. 125 (1930), 564.
5 Kassel, J.A.C.S. 54 (1932), 3949.
6 Meek. Z. Electrochem. 36 (1930), 589.
8 Rice and Glasebrook. ibid. 55 (1934), 2381.
10 " and Rideal, J.A.C.S. 57 (1935), 1168.
11 " " " ibid. " " 2466.
12 Rice and Dooley. ibid. 56 (1934), 2747.
16 Pearson, Purcell, and Saigh. ibid. (1938), 409.
17 Doering, Buttery, Laughlin, and Chandhury. J.A.C.S. 78 (1956), 3224.
20 " ibid. 251 (1959), 575.
21 Strachen and Noyes, J.A.C.S. 76 (1954), 3258.
23 Kistiakowsky and Rosenberg. ibid. 72 (1950), 321.
26 Kistiakowsky and Kydd. ibid. 79 (1957), 4825.
28 Heisgen, Diese Ztschr. 67 (1955), 439.
  b " " " ibid. " , 701.
31 Knox and Trotman-Dickenson. Chem. and Ind. (1957), 1039.
32 " " " ibid. (1957), 731.
33 " " " ibid. (1957), 268.
36 Franzen and Kuntze. ibid. 627 (1959), 15.
37 Franzen ibid. " " , 22.
38 Doering and Knox. J.A.C.S. 78 (1956), 4947.
40 Kharasch, Rudy, Nudenberg and Bushi. J. Org.Chem. 18 (1953), 1030.
43
44 Skell and Woodworth. J.A.C.S. 78 (1956), 4496.
45 Doering and Le Flamme, ibid. 78 (1956), 5447.
48 Doering and Hoffman. ibid. 76 (1954), 6162.
49 Kistiakowsky and Satter. ibid. 80 (1958), 1066.
50 Butler and Kistiakowsky. ibid. 82 (1960), 759.
54 Lipp and Köster, Ber 64 (1931), 2823.
57 Doering and Henderson. ibid. 80 (1958), 5274.
58 Hins and Dowell, Jr. ibid. 76 (1954), 2688.
60 Skell and Woodworth. J.A.C.S. 78 (1956), 6427.
63 Sato and Cvetanovic. ibid. 37 (1959), 953.
64 Doering and Knox. J.A.C.S. 72 (1950), 2305.
65 " " " ibid. 75 (1953), 297.
66 " " " ibid. 73 (1951), 828.
67 Saltmarsh and Norrish. J.C.S. (1935), 455.
68 Blacet and Miller. J.A.C.S. 79 (1957), 4327.
69 Strachen and Blacet. ibid. 77 (1955), 5254.
70 Ernest and Mitrab. Chem. Listy 52 (1958), 348.
73 Chanmugam and Burton. J.A.C.S. 78 (1956), 509.
74 Urry and Eiszner. ibid. 74 (1952), 5822.
76 Staudinger and Kupfer. Ber 45 (1912), 501, 504, 58.

Bramford and Dewar. J. C. S. (1949), 2877.

U. S. P. 2, 175, 611.

B. P. 472, 983.


Leermakers. J. A. C. S. 56 (1934), 1899.

Rice and Hersfeld. ibid. 284.


Trotman-Dickinson and Steacie. ibid. 19 (1951), 329.


Knox and Trotman-Dickenson. Chem. and Ind. (1957), 731.


Holroyd and Noyes. J. A. C. S. 78 (1956), 4831.


Franzen. ibid. 627 (1959), 22.