THE THERMAL DECOMPOSITION
OF THE
LOWER ALKYL HYDROPEROXIDES

Thesis
submitted for the Degree of
Doctor of Philosophy.

by
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I.

Abstract

The present state of knowledge regarding the homogeneous gas phase decompositions of the dialkyl peroxides, hydroperoxides and hydrogen peroxide is reviewed. The evidence for the occurrence of the homolytic O-O bond break is considered and the experimental difficulties encountered in studying this reaction for the hydroperoxides are described. Some initial attempts to study the thermal decomposition of hydrogen peroxide into two hydroxyl radicals using Szwarc's toluene carrier method are outlined. The thesis then deals in detail with the study of the thermal decompositions of tert-butyl, isopropyl and ethyl hydroperoxides in the temperature range 270-380°C using a benzene carrier. Definite evidence is presented for the occurrence of the reaction

$$\text{ROOH} \rightarrow \text{RO} + \text{OH}$$

as the initial, rate determining step of the decompositions. Values are obtained for the Arrhenius parameters for these reactions, the probable errors given and the possible sources of systematic error considered. The final values adopted are,

<table>
<thead>
<tr>
<th>Hydroperoxide</th>
<th>log A</th>
<th>E Kcaps/mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tert-butyl</td>
<td>13.3 - 14.3</td>
<td>37.8 ± 0.7</td>
</tr>
<tr>
<td>Isopropyl</td>
<td>14.1 - 15.1</td>
<td>40.7 ± 0.8</td>
</tr>
<tr>
<td>Ethyl</td>
<td>13.0 - 14.0</td>
<td>37.7 ± 0.8</td>
</tr>
</tbody>
</table>

For ethyl hydroperoxide an additional error of ± 3% is
II.

possible.

In the Discussion it is shown that the rates of decomposition of these hydroperoxides are too high for them to be important as degenerate chain branching agents in the low temperature, gas phase oxidation of hydrocarbons. The group energy term for the hydroperoxyl group in a hydroperoxide is calculated and the derived heat of formation for tert-butyl hydroperoxide found to be in good agreement with the experimental value. The possible use of hydroperoxides as sources of hydroxyl radical is considered and a short discussion of the magnitude of the A factors obtained in peroxide decompositions follows. In conclusion an indication is given of some of the work which remains to be done in this field.
Hydrogen peroxide, the parent substance of the organic peroxides, was discovered in 1818 by Thenard (1) during a study of the action of mineral acids on barium peroxide. Since that time a great deal of attention has been paid to it with the result that the properties of the substance are well known. Hydrogen peroxide is a colourless, weakly acidic liquid, more dense and slightly more viscous than water, with a similar melting point but a much higher boiling point (155.5°C). Although under certain conditions hydrogen peroxide may act as a reducing agent, it is a strong oxidant and as a consequence its main industrial use is as a bleaching agent. In this capacity it has the great advantage of giving harmless products.

Until recent years almost all the studies of hydrogen peroxide have been carried out in the liquid phase. In ionic systems the reactions of hydrogen peroxide can be explained by its ability to dissociate into $\text{H}^+$ and $\text{HO}_2^-$ or by the reaction,

$$\text{H}_2\text{O}_2^+e \rightarrow \text{OH} + \text{OH}^-$$

while in photolytic work the reaction,

$$\text{H}_2\text{O}_2 \rightarrow 2\text{OH}$$

may be important. Such systems are not, however, strictly relevant to the present thesis. In the Introduction an account will be given of the work carried out on the gas
phase decomposition of hydrogen peroxide. This is of two-fold interest as the original aim of the present research was a study of the homogeneous reaction

\[ \text{H}_2\text{O}_2 \rightarrow 2\text{OH} \]

and secondly, the difficulties associated with work on hydrogen peroxide illustrate the problems encountered in work on the alkyl hydroperoxides.

The organic peroxides may be represented by the formula \( \text{ROOR'} \) where \( R \) and \( R' \) may be organic groupings or hydrogen. Attention will be paid only to those peroxides where \( R \) and \( R' \) are alkyl radicals or hydrogen. For the symmetrical dialkyl peroxides \( R \) and \( R' \) are the same and for the alkyl hydroperoxides \( R' \) is a hydrogen atom. Not much work has been carried out on unsymmetrical dialkyl peroxides but a section which reviews the available information has been included in the Introduction.

The first dialkyl peroxide to be isolated was diethyl peroxide, obtained by Berthelot (2) from the products of the prolonged ozonisation of ether. In 1900 Baeyer and Villiger (3&4) developed the first preparative method, reaction of dialkyl sulphates with alkaline hydrogen peroxide, and used it to prepare diethyl peroxide, and methyl and ethyl hydroperoxides. Alternative syntheses are now known but the original method is still widely used.

In properties the dialkyl peroxides differ from the
alkyl hydroperoxides in being relatively inert, oxidising acid potassium iodide only with difficulty. The hydroperoxides on the other hand are stronger oxidising agents and are weakly acidic forming potassium and barium salts. The lower members of both series tend to be explosive and the barium salts of the hydroperoxides are particularly hazardous. The hydroperoxides do not keep well and decompose on standing. Unlike the diacyl peroxides which are widely used as polymerisation initiators the dialkyl peroxides, with the possible exception of di-tert-butyl peroxide, do not have as yet any industrial importance.

As a direct consequence of the instability of the hydroperoxides the kinetic and thermochemical data available for them is very limited. This is also true to a lesser extent for the dialkyl peroxides. The aim of this thesis is to present evidence for the thermal decomposition

$$\text{ROOH } \rightarrow \text{ RO } + \text{ OH}$$

for the alkyl hydroperoxides and hydrogen peroxide and to study the rates of decomposition of the alkyl hydroperoxides in the gas phase.

Apart from the intrinsic value of a knowledge of the rate constants for these reactions they are of interest in view of the doubt concerning the exact processes occurring in oxidation systems. The latter reactions are often of considerable complexity and this is evidenced by the
voluminous literature on the subject. This aspect of the work will be discussed more fully later but it should be noted here that many investigators believe that the alkyl hydroperoxides play an important role in oxidation reactions.

The sections which follow deal with the work carried out to date on the decompositions of the dialkyl peroxides, alkyl hydroperoxides and hydrogen peroxide. The order adopted requires some explanation. First the dialkyl peroxides have been briefly treated since, for these compounds, there is clear evidence that the decomposition occurs by means of an initial O-O bond split into two alkoxy radicals. A short section on unsymmetrical dialkyl peroxides follows. The decomposition of hydrogen peroxide vapour is next considered as once more evidence is presented for the occurrence of the O-O bond split. The final section of the Introduction deals with the incomplete work for the hydroperoxides and the heterogeneous nature of their decompositions.
INTRODUCTION

2.1) DIALKYL PEROXIDES.

Di-tert-butyl peroxide (DTBP) is considered first as the most extensive work has been carried out on this peroxide. Thereafter the peroxides are considered according to their position in the series.

The main reason for the interest in the thermal decomposition of DTBP is its importance as a source of methyl radicals in the temperature region 130-170°C.

In 1943 Raley, Rust and Vaughan (5) were able to show, by studying the gas phase decomposition of DTBP, in a static system with a nitrogen diluent, that the reaction was homogeneous, first order, non-chain and occurred by means of an initial O-O bond split giving rise to two tert-butoxy radicals. The values obtained for the Arrhenius parameters were $E=39.1$ Kcals/mole; $A=3.2 \times 10^{16} \text{sec}^{-1}$. Two sets of experiments were carried out by Murawski, Roberts and Szwarc (6) using a static method and the toluene carried method. The activation energies and $A$ factors obtained in both experiments were significantly lower than those of Raley, Rust and Vaughan ($E'_s=34$ & 36 Kcals/mole; $A'_s=4-7 \times 10^{14} \text{sec}^{-1}$.)

Subsequent studies by Jaquiss, Roberts and Szwarc (7); Brinton and Volman (8); and Pritchard, Pritchard and Trotman-Dickenson (10) using static systems and a mass
spectrometric investigation by Lossing and Tickner (9) confirm the findings of Raley, Rust and Vaughan as to the nature of the reaction, although varying values were obtained for the activation energy and A factor. The rate constants for the decomposition of DTBP in solution in cumene, tert-butyl benzene and tri-n-butylamine have been found to be similar to the values for the gas phase reaction (11). This indicates the operation of the same rate controlling step in both circumstances.

Table 1 lists the values of the Arrhenius parameters obtained in the above investigations together with an indication of the experimental method used. At the foot of this table will be found the values recommended by Hanst and Calvert in their paper on dimethyl peroxide. A slightly lower value of E=37 Kcals/mole is recommended by Gray (12) and Cottrell (13).

The lowest member of the series, dimethyl peroxide, was first examined by Takezaki and Takeuchi (14) in 1954. They found that the peroxide decomposed homogeneously following a first order law. Later Hanst and Calvert (15) confirmed these findings and gave a similar value for the activation energy of the rate determining step. Takezaki and Takeuchi studied the decomposition in an excess of methanol vapour while Hanst and Calvert used the pure peroxide vapour. The two systems therefore differed in the second step of the
reaction but both investigators agreed that the rate determining process was the fission of the O-O bond.

A study of the decomposition of diethyl peroxide was carried out by Harris and Egerton (16). Using a static system the rate constants of the slow decomposition and also the critical explosion limits were measured. It was shown that different products were obtained from the two types of reaction. The slow reaction was shown to be first order after an initial induction period and was unaffected by the surface or shape of the reaction vessel. These workers found $E=31.5 \text{ Kcals/mole}$ and $A=5.1 \times 10^{14} \text{ sec}^{-1}$.

Moriya (17), in 1948, also studied both the slow and explosive decompositions in a static system. Although the rates were unaffected, the final pressure increase was found to vary with the reaction vessel shape. Moriya also found the reaction to be first order after an induction period. This was increased on addition of nitric oxide and 50% nitric oxide inhibited the reaction completely suggesting that chain reaction was occurring. The fact that explosive decomposition occurred is further evidence of this. It was not appreciated by either of these workers that a chain mechanism could be consistent with first order kinetics. Therefore both concluded that no chains in fact occurred. Moriya's results are contradictory as he found the same activation energy with and without nitric oxide; $E=29.9 \text{ Kcals/mole}$ and $A=1.1 \times 10^{12} \text{ sec}^{-1}$. 
<table>
<thead>
<tr>
<th>Peroxide</th>
<th>Method Used</th>
<th>( E ) Kcals/mole</th>
<th>( A ) sec(^{-1} )</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Di-t-amyl</td>
<td>Static, ( N_2 ) as diluent.</td>
<td>37.4</td>
<td></td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>&quot; Static, toluene as diluent.</td>
<td>34.4</td>
<td>4.7 \times 10^{14}</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>&quot; Toluene carrier flow system.</td>
<td>36.4</td>
<td>4.7 \times 10^{14}</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>&quot; Static, acetone as diluent.</td>
<td>37.4</td>
<td></td>
<td>7</td>
</tr>
<tr>
<td></td>
<td>&quot; Static, ethylenimine present.</td>
<td>36.4</td>
<td>6 \times 10^{14}</td>
<td>8</td>
</tr>
<tr>
<td></td>
<td>&quot; Flow He carrier, plus (5) &amp; (6).</td>
<td>38.4</td>
<td>7 \times 10^{15}</td>
<td>9</td>
</tr>
<tr>
<td></td>
<td>&quot; Static, ketones as diluents.</td>
<td>39.4</td>
<td>4 \times 10^{16}</td>
<td>10</td>
</tr>
<tr>
<td>Di-n-propyl</td>
<td>Static</td>
<td>36.5</td>
<td>2.5 \times 10^{15}</td>
<td>19</td>
</tr>
<tr>
<td>Diethyl</td>
<td>Static, with He, ( H_2, CO_2, NO, air.</td>
<td>31.5</td>
<td>5.1 \times 10^{14}</td>
<td>16</td>
</tr>
<tr>
<td></td>
<td>&quot; Static, with ( O_2, H_2, Me_4Pb, NO.</td>
<td>29.9</td>
<td>1.1 \times 10^{12}</td>
<td>17</td>
</tr>
<tr>
<td></td>
<td>&quot; Flow, toluene carrier.</td>
<td>31.7</td>
<td>2 \times 10^{13}</td>
<td>18</td>
</tr>
<tr>
<td>Dimethyl</td>
<td>Static, in presence of ( CH_3OH.</td>
<td>36.9</td>
<td>4 \times 10^{15}</td>
<td>14</td>
</tr>
<tr>
<td></td>
<td>&quot; Static, pure peroxide vapour.</td>
<td>35.3</td>
<td>1.6 \times 10^{14}</td>
<td>15</td>
</tr>
</tbody>
</table>

**RECOMMENDED VALUES (Hanst & Calvert) (15)**

| Peroxide       | Method Used                                 | \( E \) Kcals/mole | \( A \) sec\(^{-1} \) |
|---------------|---------------------------------------------|--------------------|----------------|------|
| Di-t-butyl    | Ave. of (5) & (6).                          | 37.5               | 4 \times 10^{15}  |      |
| Di-n-propyl   | Harris                                      | 36.5               | 2.5 \times 10^{15} |      |
| Diethyl       | Combined Arrhenius plot (16), (17) & (18)   | 34.1               | 1.6 \times 10^{14} |      |
| Dimethyl      | Average of (14) & (15)                       | 36.1               | 2.4 \times 10^{15} |      |
The rate constants obtained in these investigations differ by a factor of about 80 at 150°C.

More recently Rebbert and Laidler (18) have carried out a study of the decomposition using the toluene carrier method. In this system there was very little possibility of chain reaction and the rate constants found were intermediate to those of the previous work. They found $E=31.7$ Kcals/mole and $A=2\times10^{13}\text{sec}^{-1}$, the rate determining step being the $0-0$ bond split.

Harris has also examined di-β-propyl peroxide using a static system and obtained $E=36.5$ Kcals/mole and $A=2.5\times10^{15}\text{sec}^{-1}$ for the $0-0$ bond split in this molecule.

Finally, Raley, Rust and Vaughan (5) studied the decomposition of di-tert-amyl peroxide and found the activation energy to be approximately the same as for DTBP.

The results of all this work have been listed in Table 1.

In general therefore the dialkyl peroxides decompose thermally by a homogeneous, first order reaction, the rate determining step being the split of the $0-0$ bond giving rise to two alkoxy radicals.

$$\text{i.e.} \quad \text{ROOR} \rightarrow \text{RO} \quad + \quad \text{RO}$$

Under suitable conditions the subsequent reactions of the alkoxy radicals do not lead to chains.

Comparison of the five peroxides for which data are
available shows that the activation energy is almost constant but falls slightly on descending the series. However diethyl peroxide is anomalous in this respect. For this reason Hanst and Calvert reinvestigated dimethyl peroxide believing that the value for this peroxide might be high. On obtaining the same value as Takezaki and Takeuchi for dimethyl peroxide, they obtained a revised value of $E=34.1$ Kcal/mole for diethyl peroxide from a combined Arrhenius plot of the work of Harris and Egerton; Moriya; and Rebbert and Laidler. The values recommended by Hanst and Calvert are listed at the foot of Table 1. Calculation of the rate constants at $187^\circ C. (450^\circ A)$ (about the mean temperature of the experiments) for these peroxides shows that the rates of decomposition are all very similar, viz.

\[
\begin{align*}
\text{DTBP} & : \quad k=2.5 \times 10^{-3} \text{ sec}^{-1} \\
\text{Di-n-propyl} & : \quad k=6.3 \times 10^{-3} \text{ sec}^{-1} \\
\text{Diethyl} & : \quad k=7.8 \times 10^{-3} \text{ sec}^{-1} \\
\text{Dimethyl} & : \quad k=6.3 \times 10^{-3} \text{ sec}^{-1} 
\end{align*}
\]

2.2) UNSYMMETRICAL DIALKYL PEROXIDES.

Work on unsymmetrical peroxides is limited to a qualitative study by Rust, Seubold and Vaughan (20) of the decompositions of methyl tert-butyl; ethyl tert-butyl; isopropyl tert-butyl; isobutyl tert-butyl; n-butyl tert-butyl and di-tert-butyl peroxides in cyclohexene vapour.
The purpose of this study was to determine the order of stability of the derived alkoxy radicals. Gray (12) tabulates a value of $E=36$ Kcals/mole for the decomposition of ethyl tert-butyl peroxide, this being the result obtained in an unpublished study by Style and Harrison.

2.3) HYDROGEN PEROXIDE.

Hydrogen peroxide, which may be regarded as the lowest member of the hydroperoxide series, has been the subject of a great number of investigations. Most of this work has been concerned with the decomposition of hydrogen peroxide solutions by metallic ions, light, nuclear radiations and heat while little work has been done on hydrogen peroxide vapour.

In 1932, by a study of the oxidation of hydrogen and carbon monoxide by hydrogen peroxide, von Elbe (21) was able to show that the reaction,

$$ \text{H}_2\text{O}_2 \rightarrow 2 \text{ OH} $$

occurred under the influence of light. Only in recent years, however, has direct evidence become available for this reaction in the thermal decomposition. This has been due mainly to the rapid heterogeneous decomposition of hydrogen peroxide on almost any surface and the difficulty of suppressing this reaction to any marked extent. Recently, much attention has been directed towards the homogeneous
decomposition and a paper by Hoare, Protheroe and Walsh, correlates, in a fairly satisfactory manner, the hitherto somewhat conflicting data.

Owing to the readiness with which hydrogen peroxide undergoes heterogeneous decomposition all the early investigations dealt with this. The chief characteristic of this work was the lack of agreement between the various investigators. Hinshelwood and Pritchard (22) found that, at 76°C, the decomposition was first order on glass while Elder and Rideal (23), finding the reaction irreproducible on glass, studied the decomposition on quartz at 85°C. They found it to be zero order and inhibited by oxygen, the reaction stopping after about 20% decomposition. These results were disputed by Kistiakowsky and Rosenberg (24) who, working at temperatures of 85 and 98°C, were unable to reproduce the phenomena reported by Elder and Rideal. They showed that the reaction was heterogeneous and had an almost negligible temperature coefficient. They also found that the reaction rates increased with time due to aging of the reaction vessel surface. This latter observation has since been confirmed by several investigators.

In 1946 Mackenzie and Ritchie (25) showed that, at low pressures (<1 mm.), the order of the reaction depended on the reaction vessel used and on the pressure. In addition the reaction was inhibited by water vapour and by oxygen and
nitrogen at pressures greater than 10 mm. The activation energies found varied from 4-8 Kcals/mole. In a study by Baker and Ouellet (26) the reaction was shown to be heterogeneous and first order up to 140°C while above this temperature the situation became more complex. Unlike Mackenzie and Ritchie they found that the reaction was unaffected by air, carbon dioxide or water vapour but the marked effect of the reaction vessel size and shape was again noted. Baker and Ouellet also found that Pyrex reaction vessels which had been cleaned and then fused to redness in a flame were much more inert than soda glass. Above 120°C the temperature coefficient of the decomposition became negligible. The apparent activation energies found in this work lay between 13.5 and 18.5 Kcals/mole. Kondrat'eva and Kondrat'ev (27) studied the decomposition by flowing air saturated with hydrogen peroxide vapour through both clean and salt coated glass tubes. They reported that the amount of hydrogen peroxide recovered was independent of the initial concentration and concluded that the reaction was bimolecular. This conclusion does not follow and the experimental results cannot be explained in this way. The activation energy found was 8.5 Kcals/mole.

Following on from the work of Baker and Ouellet, Giguere (28), in 1947, undertook an investigation of the effect of the nature of the reaction vessel surface on the decomposition.
The pressures used were in the region of 5-6 mm. Hg and the
temperature range 50-420°C. The vessels used were one litre
flasks in soft glass, Pyrex and quartz, some being metall-
ised. These were pretreated in various ways; acid washing,
salt coating, etching with hydrofluoric acid and fusing in a
flame. While in most cases first order decompositions were
observed, the treatments had a marked effect on the re-
action rate and hydrofluoric acid etching led to erratic
results. Giguerre concluded that the decomposition of
hydrogen peroxide was completely heterogeneous up to 420°C.
The activation energies obtained lay in the range 8-20 Kcals/
mole.

This work shows that the result of any investigation
into the heterogeneous decomposition of hydrogen peroxide
depends almost entirely on the size and shape of the reac-
tion vessel used, the material of which it is constructed
and its treatment prior to the experiments.

Thus, in 1949, when McLane (29) undertook his invest-
igation of the high temperature decomposition of hydrogen
peroxide vapour, none of the direct evidence then available
indicated the occurrence of a homogeneous reaction. This
was due to the rapidity of the heterogeneous reaction.
Mclane found it possible to reduce the surface activity of
his reaction vessels by coating with boric acid. Then,
by using a flow system giving low contact times of about
1-5 secs with oxygen and nitrogen carrier gases at pressures of one atmosphere, the heterogeneous reaction was slowed down sufficiently for the homogeneous reaction to become important. Runs were carried out in two types of reaction vessel. Firstly experiments were carried out in a set of reaction vessels (surface/volume = 7 cm⁻¹) constructed from 8 mm. diameter tubing, the contact time being altered by varying the length of the tubing. End effects were avoided by using the same inlet and outlet tubes and by keeping the flow rate constant. The second set of experiments was carried out in a mixed reactor of surface/volume 3 cm⁻¹. In both experiments the inlet and outlet concentrations of hydrogen peroxide were measured photometrically.

The results showed that while the first order rate constants were not strongly dependent on the surface/volume ratio some surface reaction was still occurring. An activation energy of 40 Kcals/mole was obtained for both carrier gases in the experiments with the higher surface reaction vessels. Unfortunately not much data was obtained for the mixed reactor but results with nitrogen gave an activation energy of 50 Kcals/mole. The increase in activation energy points to a contribution from the heterogeneous reaction in the higher surface vessels. McLane felt that the temperature range used, 470-540°C, was too restricted to show the curvature in the Arrhenius plot due
to this. The activation energy recommended was therefore the higher value.

Such was the situation at the beginning of the present work in 1956. Since then several papers have appeared which have greatly clarified the subject.

In 1957 Giguere and Liu (30) studied the decomposition in a static system. The information gained from the studies of the heterogeneous reaction enabled surfaces of low catalytic activity to be prepared by careful cleaning with hot, fuming sulphuric acid and either fusing in a flame or treating with concentrated hydrogen peroxide. In Vycor flasks treated in this manner the homogeneous reaction was detected at 400°C and it was possible to follow the decomposition up to 600°C. Unlike McLane these workers found boric acid coatings unsatisfactory. Packing of the reaction vessel with glass rods and addition of inert gases and nitric oxide and propylene had little effect on the reaction above 400-425°C. It was therefore concluded that in this region the decomposition was essentially a homogeneous, non-chain reaction which was furthermore shown to be first order. The rate constants were, however, corrected for the residual heterogeneous reaction, the correction becoming small above 430°C. This was done by extrapolation of the Arrhenius curve for the heterogeneous reaction and subtraction of the rate constants obtained from the total
rate constant. The final rate constant obtained was given by the equation,

$$k = 10^{13} \exp\left(-\frac{48,000}{RT}\right) \sec^{-1}$$

The A factor is the value that would be expected for a "normal" first order decomposition ($\frac{kT}{h}$) and E is close to the thermochemical heat of dissociation of hydrogen peroxide ($D(HO-OH) = 48.5$ Kcals/mole (30)).

Giguere and Liu also calculated the region of fall off of the first order rate constants for hydrogen peroxide to be about 75 mm. using the equation derived by Benson (31). This appeared to be of the observed order, the uncertainty being due to the predominance of the heterogeneous reaction at low pressures.

Satterfield and Stein (32) examined the reaction using a flow system, the reactant mixture consisting of water vapour containing varying percentages of hydrogen peroxide at a total pressure of one atmosphere. The reaction was studied in the temperature range 215-490°C and, in agreement with Giguere and Liu, a transition from heterogeneous to homogeneous reaction occurred in the region 400-450°C. The partial pressures of hydrogen peroxide used were in the range 0.4-20 mm. Hg (0.0006-0.029 atmos.) and the data obtained indicated order of 1.5 for the decomposition. This order was used to correct the rate constants to 15 mm. Hg and
thus an activation energy of 55 Kcals/mole was obtained. The results were interpreted in terms of a chain mechanism of the type,

Initiation \( H_2O_2 + M \rightarrow 2 OH + M \) \( (1) \)

Chaining \( OH + H_2O_2 \rightarrow H_2O + HO_2 \) \( (2) \)
\( HO_2 + H_2O_2 \rightarrow H_2O + O_2 + OH \) \( (5) \)

Termination \( 2 OH + M \rightarrow H_2O_2 + M \) \( (6a) \)
\( OH + HO_2 + M \rightarrow O_2 + H_2O + M \) \( (6b) \)
\( 2HO_2 + M \rightarrow H_2O_2 + O_2 + M \) \( (6c) \)

This scheme results in a three halves order rate expression if one or more of the radical/radical reactions is the main chain terminating step. These results contrast with those of Giguere and Liu who found the reaction to be non-chain and first order.

The conclusions reached by Satterfield and Stein were criticised by Conway (33). According to their scheme the overall activation energy \( E_t \) is given by

\[ E_t = \frac{1}{3}(E_1 - E_6) + E_2 \]

\( E_1 - E_6 \) is probably no greater than 43 Kcals/mole. Therefore \( E_2 \) would have to have the abnormally high value of 31 Kcals/mole. Conway further pointed out that, allowing for the presence of heterogeneous reaction, Satterfield and Stein's rates were of the same order as those found by Giguere and Liu.

It is apparent from the results of Giguere and Liu and
Satterfield and Stein that the decomposition of hydrogen peroxide is a unimolecular reaction in its second order region at the pressures used. This possibility was discussed by the former workers but they regarded their results as too crude to provide any definite information. More detailed experimental evidence is now available. Forst (34), in 1958, examined the decomposition statically at pressures up to 22 mm. Hg and in the presence of added helium, oxygen and water vapour to total pressures of up to 100 mm. Hg. The first order rate constants were found to vary linearly with inert gas pressure at constant hydrogen peroxide concentration and with hydrogen peroxide concentration at constant inert gas pressure. The reaction was studied over the temperature range 430-470°C. It was found that helium inhibited the heterogeneous reaction completely. It was therefore possible to correct the rate constants for the pure peroxide decomposition for the heterogeneous contribution. The second order rate constants were then in accord with the equation,

\[ k = 10^{15} \exp\left(\frac{-48,000}{RT}\right) \text{ litre mole}^{-1}\text{ sec}^{-1} \]

Similar values were obtained for activation by helium. No departure from the linear relationship of the first order rate constant with pressure was observed at the highest pressures used in this work (90 mm. Hg). This indicates
that Giguere and Liu's estimate of the fall off region is too low.

The most recent paper to appear is by Hoare, Protheroe and Walsh (35) and in this an attempt has been made to correlate the results of the previous investigations with their own work. A flow system was used and runs were carried out both at atmospheric and at lower pressures, the pressures of peroxide varying between 0.1 and 5 mm. Hg. The temperature range for the high pressure work was 241-478°C and for the low pressure, 569-659°C. The transition point from heterogeneous to homogeneous reaction again lay in the region of 420°C. Both the heterogeneous and homogeneous reactions were shown to be first order and the pressure dependence of the rate constant was demonstrated up to one atmosphere. Various gases were used as inert bodies and an order of efficiencies, hydrogen peroxide > water > carbon dioxide > nitrogen > oxygen > helium was established. The explanation given for the high efficiencies of hydrogen peroxide and water was that energy transfer can take place more readily when the energy states in the colliding molecules are similar.

Hoare, Protheroe and Walsh recalculated the results of McLane, Satterfield and Stein, and Giguere and Liu assuming first order dependence of the rate on both the hydrogen peroxide pressure and the inert gas pressure, allowing for
the different efficiencies of the gases. The second order rate constant thus obtained was, for activation by peroxide,
\[ k = 10^{15.4} \exp\left(-\frac{48000}{RT}\right) \text{litre mole}^{-1} \text{sec}^{-1}. \]
in good agreement with Forst's value.

The conclusion that the first order rate constants are pressure dependent up to at least one atmosphere is supported in a recent paper by Gill and Laidler (36). These authors have carried out a vibrational analysis of the hydrogen peroxide molecule and have shown that the pressure at which the rate constant attains half its value at infinite pressure is likely to be of the order of several atmospheres.

It may be concluded that under favourable conditions the decomposition of hydrogen peroxide occurs by a homogeneous, first order mechanism. The most probable sequence of reaction is,

\[
\begin{align*}
H_2O_2 + M & \rightarrow 2 OH + M \quad (1) \\
OH + H_2O_2 & \rightarrow H_2O + HO_2 \quad (2) \\
HO_2 + HO_2 & \rightarrow H_2O_2 + O_2 \quad (3)
\end{align*}
\]

Other possible reactions can be discounted.

There is strong evidence in favour of reaction (1) occurring as the initial step of the decomposition, the only other possible reaction being,

\[
H_2O_2 + M \rightarrow HO_2 + H + M
\]

This reaction is very unlikely as \( \Delta(HO_2 - H) \) is of the order of 90 Kcals/mole (37). Further hydroxyl radicals have
been shown to be produced in the photolytic decomposition of hydrogen peroxide (38) and in electrical discharge studies (39).

2.4) ALKYL HYDROPEROXIDES.

As with hydrogen peroxide work on the gas phase, homogeneous decomposition of the alkyl hydroperoxides has been hampered by their ready heterogeneous decomposition. In addition these compounds are fairly involatile and decompose in the liquid phase if heated. Further difficulties are the very poor preparative yields, the difficulty of purification and the explosive nature of the compounds. Thus the reliable information on the decomposition of these compounds in the gas phase is rather limited.

No direct evidence existed in 1957 for the occurrence in the gas phase of the homolytic O-O bond split except for tert-butyl hydroperoxide. Solution work on the higher alkyl hydroperoxides does, however, indicate that this process occurs. Thomas (40) has studied the decompositions in white oil solution of tetracyl, α-cumyl, n-octyl and 2, 4, 4, trimethyl pentyl-2 hydroperoxides. Similar work has been carried out on the decompositions of cyclohexyl hydroperoxide in cyclohexane (41), decalyl hydroperoxide in decalin (42), sec-decalyl hydroperoxide in n-decane (43) and tert-butyl hydroperoxide in n-octane. All these decompositions were
<table>
<thead>
<tr>
<th>Hydroperoxide</th>
<th>$E$ Kcals/mole</th>
<th>$A$ $\text{sec}^{-1}$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tetralyl</td>
<td>29</td>
<td>$1.3 \times 10^{11}$</td>
<td>40</td>
</tr>
<tr>
<td>$\alpha$-Cumyl</td>
<td>29</td>
<td>$1.3 \times 10^{11}$</td>
<td>40</td>
</tr>
<tr>
<td>n-Octyl</td>
<td>26.9</td>
<td>$1 \times 10^{10}$</td>
<td>40</td>
</tr>
<tr>
<td>2, 4, 4 Trimethyl Pentyl-2</td>
<td>26.9</td>
<td>$1 \times 10^{10}$</td>
<td>40</td>
</tr>
<tr>
<td>t-Butyl</td>
<td>39.0</td>
<td>$1.2 \times 10^{15}$</td>
<td>44</td>
</tr>
<tr>
<td>Cyclohexyl</td>
<td>34.0</td>
<td>$1.2 \times 10^{13}$</td>
<td>41</td>
</tr>
<tr>
<td>Decalyl</td>
<td>32.1</td>
<td>$8.5 \times 10^{13}$</td>
<td>42</td>
</tr>
<tr>
<td>Sec-Decalyl</td>
<td>31.7</td>
<td>$1 \times 10^{12}$</td>
<td>43</td>
</tr>
</tbody>
</table>
first order; the activation energies obtained are listed in Table 2 and are thought to be those for the O-O bond split. The values are similar to those for the gas phase decompositions of the lower dialkyl hydroperoxides. Thomas, therefore suggests that the influence of the alkyl substituents on the peroxide bond strength may be small. The interpretation of the solution results may not, however, be completely unambiguous, although an exception may be made for Thomas's experiments which were carried out in the presence of sufficient inhibitor to prevent secondary reactions.

The decomposition of tert-butyl hydroperoxide was examined in n-octane solution by Bell, Haley, Rust, Seubold and Vaughan (44) and was shown to be complex, being a combination of unimolecular and chain processes. Consequently the rate constants for the unimolecular reaction were obtained by extrapolation of the overall rate constants to zero concentration. A value of $E = 39.0$ Kcals/mole was thereby obtained. This value is the same as for DTBP, once more indicating that the substituents do not have a large effect on the O-O bond strength.

Table 2 shows A's and E's for these eight hydroperoxides. While the activation energies vary significantly the actual rate constants in the temperature range studied are very similar. The rate constants at $450^\circ$A have been calculated
and are listed below.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Rate Constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tetralyl Hydroperoxide</td>
<td>$1 \times 10^{-3}$ sec$^{-1}$</td>
</tr>
<tr>
<td>α-Cumyl</td>
<td>$1 \times 10^{-3}$ sec$^{-1}$</td>
</tr>
<tr>
<td>n-Octyl</td>
<td>$8 \times 10^{-4}$ sec$^{-1}$</td>
</tr>
<tr>
<td>2, 4, 4-Tetralyl Hydroperoxide</td>
<td>$8 \times 10^{-4}$ sec$^{-1}$</td>
</tr>
<tr>
<td>Trimethyl Pentyl-2</td>
<td>$3 \times 10^{-4}$ sec$^{-1}$</td>
</tr>
<tr>
<td>t-Butyl</td>
<td>$1.6 \times 10^{-4}$ sec$^{-1}$</td>
</tr>
<tr>
<td>Cyclohexyl</td>
<td>$4 \times 10^{-4}$ sec$^{-1}$</td>
</tr>
<tr>
<td>Decalyl</td>
<td>$2 \times 10^{-2}$ sec$^{-1}$</td>
</tr>
<tr>
<td>Sec-decalyl</td>
<td>$4 \times 10^{-4}$ sec$^{-1}$</td>
</tr>
</tbody>
</table>

These values, with the exception of decalyl hydroperoxide, all lie within a factor of ten. Comparison of these rate constants with those for the dialkyl peroxides at the same temperature shows that, in general, the dialkyl peroxides decompose about ten times as fast. On the assumption of equal A factors for the two reactions this corresponds to a difference in activation energy of about 2 Kcals/mole between the peroxides and hydroperoxides. This constitutes further evidence against large effects due to substituent groupings.

The quantitative data relating to the decomposition of the alkyl hydroperoxides by the reaction

$$\text{ROOH} \rightarrow \text{RO} + \text{OH}$$

is limited to the solution studies just described. The work carried out in the gas phase has been almost entirely
concerned with the heterogeneous decomposition. There is, however, evidence that, for tert-butyl hydroperoxide the homolytic O-O bond split may occur in the gas phase.

Milas and Surgenor (45) investigated the products of the decomposition of tert-butyl hydroperoxide vapour at 250°C. Under these conditions the reaction was explosive producing acetone, methanol, tert-butyl alcohol, formaldehye and water. Bell, Raley, Rust, Seubold and Vaughan (44) carried out a more detailed study of the reaction, pyrolysing the hydroperoxide in a stream of cyclohexene. The products were acetone, tert-butyl alcohol, methane, methyl alcohol, carbon monoxide, water and cyclohexyl alcohol. These products are strong evidence of an O-O bond split followed by reaction of tert-butoxy and hydroxyl radicals. In a further study of the decomposition, Seubold, Rust and Vaughan (46) used a nitrogen carrier flow system. The results of these experiments indicated the occurrence of a chain reaction involving the tert-butoxy radical, in agreement with the solution work. At 195°C the decomposition of tert-butyl hydroperoxide was initiated by addition of DTBP, showing that the hydroperoxide was more stable at this temperature and confirming the presence of chains. It therefore appears that tert-butyl hydroperoxide has either a higher activation energy or a lower A factor.

The decomposition of tert-butyl hydroperoxide has been
treated first as the most extensive evidence concerns this member of the series. The lower hydroperoxides have been much less studied.

A study of the lowest member of the series, methyl hydroperoxide, was carried out in 1935 by Medvedev and Podyapolskaya (47) in the temperature range 200-600°C. A stream of nitrogen was used as carrier gas, the mixture being passed through a heated tube. The products found were methanol, dimethyl ether, formaldehyde, formic acid, oxygen, carbon monoxide, carbon dioxide, and water; no hydrogen or methane was detected. While most of these products may be explained by a homogeneous split of the O-O bond and the subsequent reactions of methoxy and hydroxyl radicals, it is difficult to explain the production of dimethyl ether in this way. Since no methane was found it is almost certain that methyl radicals were absent. Thus the dimethyl ether was probably formed heterogeneously, together with oxygen. Medvedev and Podyapolskaya concluded that simultaneous unimolecular and bimolecular reactions occurred, having activation energies of 11 Kcals/mole and 25 Kcals/mole respectively. It is more likely, however, that a heterogeneous process occurred along with a homogeneous, possibly chain decomposition. This would explain the observed rise in activation energy as the temperature was raised.

Harris (19) describes experiments on the decompositions
of ethyl and n-propyl hydroperoxides. He found that both decomposed heterogeneously in the temperature range 150-180°C, the decompositions being more rapid in packed or salt coated reaction vessels. However, both hydroperoxides were found to explode if suddenly heated to about 200°C indicating that a homogeneous, chain reaction could in fact occur. Further the pressure increase for the explosive decompositions was very much greater than for the heterogeneous reaction. In contrast to the corresponding dialkyl peroxides the explosion pressure for n-propyl hydroperoxide was greater than that for ethyl hydroperoxide.

Summarising, although there is some evidence that homogeneous gas phase decomposition of the alkyl hydroperoxides can occur by means of an O-O bond split, this reaction is masked by the ready heterogeneous decomposition except for tert-butyl hydroperoxide.
3.) THE AIM OF THE RESEARCH.

It has been shown in the Introduction that the evidence in favour of the gas phase decomposition of the lower alkyl hydroperoxides by the reaction,

$$\text{ROOH} \rightarrow \text{RO} + \text{OH}$$

is mostly indirect.

The aim of the present research was to study these reactions and, if possible, to obtain values for the activation energies and $A$ factors.

Initially the work was concerned with the decomposition of hydrogen peroxide but, as data became available and it was realised that the method used was not convenient for this study, attention was confined to the hydroperoxides.

The importance of the alkyl hydroperoxides lies largely in their suggested role in oxidation reactions. In addition to this however, knowledge of the bond strengths in these molecules would be of general interest. There is also the question of the high $A$ factors for some peroxide decompositions. It will have been noted that the $A$ factors for the decompositions of hydrogen peroxide and the dialkyl peroxides are all about $10^{-10}$ greater than would be expected ($\frac{kT}{h}$ for a normal unimolecular decomposition and $10^{11}$ litre mole$^{-1}$ sec$^{-1}$ for a bimolecular reaction). The alkyl hydroperoxides seem to be normal or low in this respect although the only available values have been obtained
in solution. Values for the gas phase decomposition would thus be of interest as definite conclusions can not be drawn from the present information.

The reactions of hydroxyl radicals have been rather neglected owing to the difficulty of obtaining a convenient radical source. If, however, the decompositions of the alkyl hydroperoxides were fully elucidated then an entry into the reactions of hydroxyl might be possible.

Finally it is possible that values for the bond dissociation energies of the hydroperoxides might be of use in calculating the heats of formation of the alkoxy radicals. These are important in many kinetic systems. At present, however, reliable thermochemical data for the lower alkyl hydroperoxides is lacking and also the most direct route to the alkoxy radical heats of formation is through the dialkyl peroxides.
4. EXP ERIMENTAL

4.1) GENERAL.

The initial aim of the work was a study of the decomposition of hydrogen peroxide using Szwarc's toluene carrier method (48). Subsequent to these experiments the decompositions of tert-butyl, isopropyl and ethyl hydroperoxides were studied by a similar method using benzene as carrier. Before discussing this later work, however, a brief description will be given here of the early work on hydrogen peroxide. This illustrates the principle of the method and outlines the difficulties which led to the adoption of benzene as carrier gas for the hydroperoxide work.

The toluene carrier method depends on the relative ease of abstraction of a hydrogen atom from the methyl group in toluene and the low reactivity of the resonance stabilised benzyl radical produced. Thus under suitable conditions free radicals are removed from the system on production and the resulting benzyl radicals dimerise to dibenzyl outside the main reaction zone. Estimation of the dibenzyl produced then enables the extent of the primary dissociation to be determined. For hydrogen peroxide,

\[
\begin{align*}
\text{H}_2\text{O}_2 & \rightarrow 2 \text{OH} \\
\text{OH} + \text{C}_7\text{H}_9 & \rightarrow \text{C}_7\text{H}_8 + \text{H}_2\text{O}
\end{align*}
\]
Szwarc (49) pointed out that the success of the method depends on the reaction of every radical with toluene. This confines the method to substances which give rise to reactive radicals or which have high bond dissociation energies. An upper temperature limit is set by the decomposition of the toluene itself (c.a. 800°C).

The experimental procedure is to inject a low concentration of the radical source into a stream of toluene vapour, the mixture being passed through a heated reaction vessel. The dibenzyl is usually estimated by collecting in a trap and weighing. This procedure was used in the present work.

The flow system used for the hydrogen peroxide experiments was similar to that described later. It was found, however, that the low vapour pressure of hydrogen peroxide, combined with its ready decomposition on heating, prevented capillary injection. The apparatus was therefore redesigned with a pick-up U-tube into which a small sample of 99% hydrogen peroxide was measured at the start of a run. This procedure introduced three sources of error. The duration of the run was difficult to determine with any degree of accuracy; secondly the concentration of hydrogen peroxide vapour was unknown and finally the poor vacuum at the start of a run resulting from this procedure interfered with the
estimation of the heterogeneous reaction by oxygen measurement.

In addition to the injection difficulties preliminary results indicated that, even at temperatures as low as 230°C, almost 70% of the hydrogen peroxide was decomposing heterogeneously. Unsuccessful attempts were made to reduce this by boric acid coating of the reaction vessel and all the ancillary tubing.

A further difficulty was experienced in the estimation of the dibenzyl. Calculation showed that, owing to the vapour pressure of dibenzyl at the trap temperature of -10°C (the log \( P_v \) curve was extrapolated to obtain a value of about \( 10^{-3} \) mm. at this temperature) a loss of at least 4 mg. was likely to occur in a typical run. Since the quantities of dibenzyl collected were expected to lie in the region of 5-30 mg, such a loss would be serious.

Attempts were made to eliminate this error by trapping the toluene, unchanged hydrogen peroxide and dibenzyl together at -80°C and analysing the toluene solution for dibenzyl. Two methods were tried, gas chromatography and ultra-violet spectroscopy. The first was too insensitive at the dilutions concerned while U.V. spectroscopy gave erratic results due probably to the presence of water in the solutions. It was concluded that weighing was the most accurate method of estimation available.
Preliminary results showed that dibenzyl was produced by pyrolysis of hydrogen peroxide in toluene at a temperature of 600°C. This is good evidence in favour of the occurrence of reactions \( a \), \( b \) and \( c \). It was apparent, however, that it would be extremely difficult to obtain accurate rate constants using this method.

It was therefore decided to study the decompositions of the alkyl hydroperoxides. Organic radicals such as methyl may abstract hydrogen from toluene at temperatures of 300-400°C. In view of this it was thought that, if hydroxyl was sufficiently reactive to abstract hydrogen from benzene at these temperatures, this might be used as carrier with advantage. At 350°C the relative rate of hydrogen abstraction by methyl from these two hydrocarbons is,

\[
\frac{k_{C_6H_5CH_2}}{k_{C_6H_6}} = \frac{1.3 \times 10^8}{1.6 \times 10^7} = 8 \quad (50)
\]

Preliminary experiments were carried out, pyrolysing hydrogen peroxide in benzene vapour at 600°C and tert-butyl hydroperoxide at 400°C. In both cases diphenyl was produced. A study of the decompositions of the lower alkyl hydroperoxides was therefore undertaken using benzene as carrier gas. It was hoped that the reactions occurring would be,

\[ \text{ROOH} \longrightarrow \text{RO} + \text{OH} \]
\[
\text{OH} + \text{C}_6\text{H}_6 \rightarrow \text{H}_2\text{O} + \text{C}_6\text{H}_5
\]

\[
\text{RO} \rightarrow \text{products}
\]

\[
\text{C}_6\text{H}_5 + \text{C}_6\text{H}_5 \rightarrow (\text{C}_6\text{H}_5)_2
\]

Mechanistic details for each hydroperoxide will be discussed in the appropriate section.

It should be realised that the adoption of benzene as carrier gas did not alleviate the problems associated with the measurement of the solid product, diphenyl. In fact the vapour pressure of diphenyl is higher than that of dibenzyl. This was counteracted by the fact that it was found possible to lower the trap temperature to \(-20^\circ\text{C}\) without condensation of benzene. The solution of this problem is described in the following section. This deals with the apparatus and experimental methods used during the work. The subsequent sections describe the results obtained for tert-butyl, iso-propyl and ethyl hydroperoxides.

4.2) APPARATUS AND PROCEDURE.

(a) Flow System.

The flow system was essentially the same as that described by Szwarz (48). This apparatus was constructed in Pyrex glass and is shown in Figure 1.

Two reaction vessels were used during the course of the work, one of silica having a volume of 87.5 cc. and one of Pyrex, volume 92.5 cc. The volumes were measured between
two points halfway along the inlet and outlet tubes.

The furnace was heated by three windings, two end windings of 50 ohms and a centre winding of 100 ohms. The two end windings were connected in series across the centre winding and thence to the output of a step-down transformer. Provision of a 650 ohm variable resistance in parallel with the hotter of the end windings and a 45 ohm variable resistance in series with the centre winding enabled the temperature profile of the furnace to be levelled until the variation of temperature along the widest part of the reaction vessel was no more than ±2°C at all temperatures up to 700°C. The furnace temperature was measured to an accuracy of ±0.25 C by a T₁/T₂ thermocouple (British Driver-Harris, Ltd.) used in conjunction with a Doran thermocouple potentiometer.

The complete flow system up to the diphenyl trap was wound with heating tape (11.77 ohms/ft.) carrying a current sufficient to raise these sections of the apparatus to about 60°C. This prevented both the condensation of vapours in the tubing and the premature condensation of diphenyl in the reaction vessel outlet tubes. This winding has been omitted from Figure 1 for the sake of clarity.

Pressure measurements were made by means of the Bourdon gauge shown in Figure 1. This was found to be the most satisfactory arrangement as the mercury manometer used
initially was rapidly attacked by the hydroperoxides. A silicone oil manometer also proved unsuitable due to solution of vapours in the oil. The Bourdon gauge used had a sensitivity of 4.65 cm/cm. Hg. The gauge was stabilised by a paddle immersed in dibutyl phthalate enabling the scale to be read to an accuracy of about 0.2 mm. At the pressures used this amounted to an error of about 5%. This, however, is a random error and is accounted for in the least squares treatment of the Arrhenius plots.

Although precautions were taken to avoid a large pressure drop during the course of a run it was found impossible to prevent the pressure falling to some extent due to cooling of the benzene. In order partially to overcome this difficulty benzene was allowed to flow for two minutes before the run itself was started by opening the hydroperoxide container. Pressure readings were then taken at 2.5 min. intervals until the end of the run at 9.5 min. The four pressure readings were then averaged and this taken as the effective pressure of the reaction.

Capillaries $C_1$ and $C_2$ (Figure 1) controlled the pressures in the system, $C_2$ the total pressure and $C_1$ the partial pressure of hydroperoxide in the vapour. Additional control was obtained by variation of the temperature of the respective containers. Apart from some preliminary runs with tert-butyl hydroperoxide at high pressure (c.a. 50 mm, $C_6H_6$)
the benzene container was maintained at 0°C by an ice bath. This gave a convenient benzene pressure of 15 mm. Temperature control of the hydroperoxide container was achieved by complete immersion in warm water. The trap temperatures indicated in Figure 1 were obtained as follows.

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>Mixture.</th>
</tr>
</thead>
<tbody>
<tr>
<td>-20</td>
<td>Salt/ice</td>
</tr>
<tr>
<td>-80</td>
<td>Solid CO₂/methylated spirits</td>
</tr>
<tr>
<td>-200</td>
<td>Liquid oxygen pump-down trap at 6-10 cm. pressure</td>
</tr>
</tbody>
</table>

The gas burette was calibrated in the usual manner by weighing the mercury contained in the bulbs. The volumes of the individual bulbs were 0.13; 6.54; 25.58 and 55.76 ml. giving total volumes of 0.13; 6.67; 32.25 and 88.01 ml. from the respective graduation marks to the tap.

The apparatus was evacuated by a two stage, gas heated, mercury diffusion pump backed by a rotary oil pump. The efficiency of the system was such that the pressure in the apparatus could be reduced to 10⁻⁴ mm. in about fifteen minutes. A second mercury diffusion pump was used, Figure 1, to pump the gaseous reaction products to the pump-down trap and gas burette.

(b) Analysis.

The determinations carried out during runs were for diphenyl, unchanged hydroperoxide, gases condensable at
-200°C and non-condensable gases. In an initial series of runs on tert-butyl hydroperoxide only the non-condensable gases were analysed. This was carried out for hydrogen, carbon monoxide and methane using a copper oxide furnace at 300°C to oxidise the hydrogen and carbon monoxide. It was assumed that the condensable gas consisted entirely of ethane. When it was found that the condensable products were complex the apparatus was redesigned to allow the complete analysis of the gaseous products using gas chromatography.

The diphenyl produced in the reaction was determined by collection in a spiral trap at -20°C and weighing. The possible loss due to the vapour pressure was theoretically of the order of 1.5 mg as a lower limit. Experiments were therefore carried out to correct for this loss. Using the same conditions of benzene pressure, flow rate and diphenyl trap temperature as in a run diphenyl was distilled from a spiral container into the diphenyl trap used on the flow system. The loss in weight of the spiral container and the gain in the diphenyl trap were then measured and the graph shown in Figure 2 obtained. Theoretically one would expect a line at 45° which should intercept the ordinate (e.g. the dotted line in Fig. 2). Despite the fact that some of the points are scattered it can be seen that the experimental line passes through the origin and the
loss of diphenyl is proportional to the amount being collected. In fact, from Figure 2,

True wt. diphenyl = 1.06 x Wt. diphenyl collected.

This equation was used to correct the run data as described later.

Hydroperoxide analyses were carried out using a simplified form of the iodometric method described by Wagner, Smith and Peters (51). (See also Koknatur and Jelling (52)). The procedure was as follows. The hydroperoxide was dissolved in isopropyl alcohol (50 ml.) and 1 ml. glacial acetic acid was added. Carbon dioxide was then bubbled through the solution for at least 15 min. 1 gm. sodium iodide was added, dissolved, the flask fitted with a Bunsen valve and the solution heated to just below boiling for 3 min. After adding 50 ml. water the resulting iodine solution was titrated with 0.1 N sodium thiosulphate solution.

The important factors in the procedure are the absence of water and oxygen during the reaction of the hydroperoxide with sodium iodide, the presence of water during the titration and the time of heating. Water appears to inhibit the reaction,

\[ 2\text{NaI} + \text{ROOH} \rightarrow \text{RONa} + \text{HONa} + \text{I}_2 \quad \text{d} \]

while the reaction,

\[ \text{I}_2 + \text{Na}_2\text{S}_2\text{O}_3 \rightarrow 2\text{NaI} + \text{Na}_2\text{S}_4\text{O}_6 \quad \text{e} \]
is slow in the absence of water. The absence of air during reaction \( d \) reduces the risk of high results due to air oxidation of sodium iodide. The time of heating of three minutes was found to be sufficient for the completion of \( d \) without causing any loss of iodine vapour.

This procedure gives excellent results with tert-butyl hydroperoxide. There is some doubt as to its efficiency with ethyl and isopropyl hydroperoxides as these were not pure and the method was used to estimate their purity on the basis of 100% reaction. Since their purity by titration agreed reasonably well with the gas chromatographic values, however, it seems that the method is probably quantitative.

The gas chromatographic apparatus was designed to analyse for hydrogen, methane, carbon monoxide, oxygen, ethane and higher hydrocarbons to \( C_4 \). For this purpose two columns were used; activated carbon for the non-condensable gases and 30% nitrobenzene/firebrick for the condensable gases. The columns were prepared as follows,

52-72 mesh Sutcliffe and Speakman No. 207B charcoal was activated by heating to 400°C under vacuum until it had been thoroughly degassed. A 4 ft. column was then packed with this material. (The packing used was prepared by J. F. Falconer).

A slurry of chloroform and firebrick was prepared using firebrick that had been graded and washed free of dust.
Nitrobenzene, 30\% by weight of the firebrick, was mixed with an equal volume of chloroform and added to the slurry with mixing. The chloroform was then removed by evacuation with a water pump. An 8 ft. column was prepared from this material.

Both columns were made in 4 ft. U-tubes of 5 mm. I.D. Pyrex tubing.

The layout of the gas chromatography apparatus was conventional and is shown in Figure 3. The columns described were arranged by means of two way taps so as to be interchangeable. Samples were taken into the chromatography U-tube (vol. 16.3 cc.) directly from the gas burette. The carrier gas was B.O.C. cylinder nitrogen dried with phosphorus pentoxide and calcium chloride.

The detector was a thermal conductivity gauge and this gauge and its related circuit are shown in Figure 3. The detector circuit is a slightly modified Wheatstone bridge with a standardised e.m.f. across it. Two amplifiers were used throughout the course of the work, a Sunvic DCA1 Mk II D.C. amplifier which was subsequently found to be faulty and a Pye D.C. microvoltmeter of the suspended galvanometer type. The recorder used throughout was a Record 0.5 ma. D.C. milliammeter having chart speeds of 6" and 12"/hour.

Estimation of gases was carried out by measurement of peak heights and the apparatus was calibrated for hydrogen,
FIGURE 3

GAS CHROMATOGRAPHY
APPARATUS
carbon monoxide, methane, oxygen, ethane, propane, propylene, and isobutene. A typical calibration curve is shown in Figure 4. The gases used for the calibrations were obtained as follows:

- **Hydrogen** B.O.G. cylinder.
- **Carbon Monoxide** Dehydration of formic acid ($c\cdot H_2SO_4$).
- **Oxygen** B.O.G. cylinder.
- **Methane** " "
- **Ethane** " "
- **Propane** I.C.I. "
- **Propylene** Dehydration isopropanol ($P_2O_5$).
- **Isobutene** " tert-butanol ($P_2O_5$)

The firebrick column did not separate ethane and ethylene so that in some runs a sample of the condensable gases was passed through a 10 ft. activated alumina column. No significant quantities of ethylene were detected.

A further column was used for the analysis and purification of the hydroperoxides. Firebrick was deactivated by coating with urea/formaldehyde resin and this material was used as a support for the dinonyl phthalate liquid phase.

**(c) Materials.**

Isopropyl alcohol was May and Baker reagent with a water content of less than 0.3%. It was not dried further.

Sodium iodide was May and Baker reagent, iodate content less than 0.0005%.
0.1N Sodium thiosulphate was prepared from Analar sodium thiosulphate and was standardised using Analar potassium iodate (53).

The benzene used as carrier gas was Analar benzene dried with sodium wire. It was found unnecessary to prepyrolyse the material as no diphenyl was produced in 'blank' runs at 600°C. The benzene was degassed by distillation into a trap at -186°C under vacuum and subsequent distillation into the container.

(d) Run Procedure.

As the run procedure was standard for all the work with the exception of some preliminary runs with tert-butyl hydroperoxide, it may be described here.

Reproducible surfaces were obtained on vessels to be weighed by cleaning the grease from joints with petrol ether and cotton wool, rinsing with water and then with acetone, and finally drying in an air blast. The vessels were then allowed to stand in the balance case for half an hour before weighing. Using this procedure it was possible to weigh the diphenyl trap to 0.1 mg.

The containers and the diphenyl trap were weighed, the apparatus assembled and evacuated. When the trap mixtures had been prepared and the traps and containers had all attained the correct temperatures, the run was started by allowing the benzene to flow for two minutes. Gases were
collected in the gas burette during this period to check on the degassing of the benzene. The hydroperoxide container was then opened and pressure readings taken at 2.5 min. intervals until the end of the run at 9.5 min. The non-condensable products were then collected in the gas burette and the tap between the mercury diffusion pump and the -80°C trap was closed. (Figure 1). Nitrogen was then admitted to the apparatus through the inlet capillary. This procedure eliminated the possibility of condensation of water in the diphenyl trap and prevented a sudden inrush of air.

The containers and trap were then prepared for weighing and the non-condensable gases measured and analysed. The gas burette was evacuated and the -200°C trap raised to -80°C to collect the condensable gases. It was necessary to maintain the trap at -80°C during this process as some material passed through the -80°C trap into the pump down trap. Even with the trap at -80°C it was found impossible to reduce the pressure to below 10⁻¹ mm. Hg, this being approximately the vapour pressure of acetone at this temperature. Thus the condensable gases contained a quantity of non-analysable material. A measured sample of the gas was therefore analysed for the absolute amount of each gas present and the amount in the total volume calculated.

The contents of the hydroperoxide/benzene trap (-80°C)
were rinsed into a conical flask with isopropyl alcohol and the unchanged hydroperoxide estimated by the procedure previously described. Finally the two containers and the diphenyl trap were weighed.

4.3) TERT-BUTYL HYDROPEROXIDE.

Purification.

It was not necessary to prepare tert-butyl hydroperoxide as it is available (Light and Co. Ltd.) in an impure form (65-70%). 250 ml. of the hydroperoxide was fractionated at reduced pressure on a 3 ft. column packed with Fenske helices. Generous fractions were discarded and a middle fraction of b.p. 38°C/16 mm. was retained. Analysis by titration showed that the purity of this material was 98.5%. In good agreement with this result a gas chromatographic determination at the end of the work indicated a purity of 98%. This is indicative of the stability of the substance at room temperature. Some of the preliminary work, Table 3, was carried out using hydroperoxide of 95% purity.

Scheme and Results.

Tert-butyl hydroperoxide was the first hydroperoxide to be studied in the present work and was selected because of its availability and stability. Preliminary experiments on the pyrolysis of hydrogen peroxide and tert-butyl
hydroperoxide in benzene, although crude, indicated that diphenyl could be produced by the reaction of hydroxyl radicals with benzene. For the tert-butyl hydroperoxide system the possible reactions are,

\[
\begin{align*}
(CH_3)_3COOH & \rightarrow (CH_3)_3CO + OH & 1 \\
(CH_3)_3CO & \rightarrow (CH_3)_2CO + CH_3 & 2 \\
OH + C_6H_6 & \rightarrow C_6H_5 + H_2O & 3 \\
C_6H_5 + C_6H_5 & \rightarrow (C_6H_5)_2 & 4 \\
C_2H_6 + CH_3 & \rightarrow C_6H_5CH_3 & 5 \\
C_6H_5 + (CH_3)_3CO & \rightarrow C_6H_5OC(CH_3)_3 & 6b \\
C_6H_5 + OH & \rightarrow C_6H_5OH & 6c \\
CH_3 + OH & \rightarrow CH_3OH & 6d \\
OH + OH + M & \rightarrow H_2O_2 + M & 6e \\
(CH_3)_3CO + OH & \rightarrow (CH_3)_3COOH & -1 \\
C_6H_6 + CH_3 & \rightarrow C_6H_5 + CH_4 & 7a \\
C_6H_6 + (CH_3)_3CO & \rightarrow C_6H_5 + (CH_3)_3COH & 7b \\
OH + (CH_3)_3COOH & \rightarrow H_2O + (CH_3)_3COO & 8a \\
CH_3 + (CH_3)_3COOH & \rightarrow CH_4 + (CH_3)_3COO & 8b \\
(CH_3)_3COO & \rightarrow (CH_3)_2CO + CH_2 + HO_2 & 9
\end{align*}
\]

The preliminary runs had shown that reaction 3 occurred to some extent. The validity of the method depends on this being rapid and reactions leading to loss or gain of phenyl or hydroxyl radicals being unimportant.

To ascertain the importance of reaction 7a the rates at
600°A of methyl radical recombination and hydrogen abstraction from benzene were calculated. The calculation is not strictly valid as the rate constant used is that obtained in the present work but an order of magnitude for the two processes is indicated.

Consider reactions 1, 2, 5 and 7a

\[ k_1 = 1 \text{ sec}^{-1} \]
\[ k_5 = 2.2 \times 10^{13} \text{ mole}^{-1} \text{ cc sec}^{-1} \]  \hspace{1cm} (54)
\[ k_{7a} = 1.2 \times 10^7 \text{ mole}^{-1} \text{ cc sec}^{-1} \]  \hspace{1cm} (55)

In a typical run,

\[ [\text{TBHP}] = \frac{\text{Moles TBHP} \times \text{Contact time}}{\text{Time of Run} \times \text{R.V. volume}} = \frac{10^{-3} \times 0.3}{450 \times 90} = 10^{-8} \text{ moles cc}^{-1}. \]

\[ [\text{C}_6\text{H}_6] = \frac{\text{PC}_{\text{C}_6\text{H}_6} \times 273 \times 10^{-3}}{760 \times 22.4 \times \text{Temp.}} = \frac{15 \times 273 \times 10^{-3}}{760 \times 22.4 \times 600} = 4 \times 10^{-7} \text{ moles cc}^{-1}. \]

In the stationary state,

\[
\frac{d [\text{CH}_3]}{dt} = k_1 [\text{TBHP}] = k_{7a} [\text{CH}_3] [\text{C}_6\text{H}_6] + k_5 [\text{CH}_3]^2
\]

\[ [\text{CH}_3] = \frac{-k_{7a} [\text{C}_6\text{H}_6] \pm \sqrt{(k_{7a} [\text{C}_6\text{H}_6])^2 + 4k_1k_5 [\text{TBHP}^2]}}{2k_5}
\]

\[ = -1.2 \times 10^7 \times 4 \times 10^{-7} \pm \sqrt{(1.2 \times 4)^2 + 4 \times 10^{-8}}
\]

\[ = -1.1 \times 10^{-13} + 2.1 \times 10^{-11}
\]

\[ = 2.1 \times 10^{-11} \text{ moles cc}^{-1}. \]

Using this value of \[ [\text{CH}_3] \]

\[ \text{RC}_2\text{H}_6 = k_5 [\text{CH}_3]^2 = 2.2 \times 10^{13} (2.1 \times 10^{-11})^2 \]
\[ RCH_4 = k_7a [CH_3] [C_6H_6] = 1.2 \times 10^7 \times 2.1 \times 10^{-11} \times 4 \times 10^{-7} \]
\[ = 10^{-10} \text{ mole cc}^{-1} \text{ sec}^{-1}. \]

Thus under these conditions the rate of recombination of methyl radicals is 100 times as fast as the rate of hydrogen abstraction from benzene. Thus the error caused by neglect of this reaction will be negligible.

Reactions 7b, 1 and 6b can be neglected as the lifetime of the tert-butoxy radical at a temperature of 600 °A would be short, (10^{-7} \text{ sec}) the activation energy of reaction 2 being only 11-16 Kcals/mole (56). This conclusion is supported by the equivalence of the ethane collected with the DTBP decomposed in Run 33, Table 4. Reactions 8a, 8b and 9 are unlikely to be significant in view of the low concentration of tert-butyl hydroperoxide present (0.3 mm. or less in 15 mm. benzene).

The remaining interfering reactions are the various recombinations listed under reaction 6. Of these recombination of hydroxyl radicals may immediately be excluded as this reaction is certainly third order (57). This may also be the case for 6d. During the course of the work it was found that no phenol was formed in the reaction. Two tests were used, the ferric chloride test and Liebermann's nitroso test with conc. sulphuric acid and sodium nitrite. It was shown that any phenol present
was less than 1% of the diphenyl collected. Sehon found phenolic material in the products of the decomposition of hydrogen peroxide in toluene vapour (communicated (30)) but this was thought to arise from the reaction,

$$\text{C}_6\text{H}_5\text{CH}_3 + \text{OH} \rightarrow \text{C}_6\text{H}_5\text{OH} + \text{CH}_3$$

Since phenol is absent from the products, reaction 6c (and by analogy 6d) can not be important.

Thus the main reactions in the system are 1, 2, 3, 4, 5 and 6a. If diphenyl is to be used as a measure of the primary dissociation of tert-butyl hydroperoxide by reaction 1 then reaction 3 must be assumed to have a very low activation energy. As this assumption is so important it will be treated fully in the Discussion. Experimental evidence in favour of this is the absence of phenol in the reaction products.

Evidence is available (58) indicating that for recombination reactions, auto- and cross-combinations occur at the statistically expected rates. Thus it appears that reaction 6a should compete strongly with reactions 4 and 5. In fact, assuming equal rates of production of phenyl and methyl radicals, one would expect twice as much toluene as diphenyl or ethane. That this was not so can readily be seen by reference to Table 4 where in many runs the ratio

$$\frac{2 \times \text{diphenyl}}{\text{TBHP, decomposed}}$$

(hereafter referred to as the fraction homogeneous reaction)
was greater than 0.5.

This shows that the extent of reaction 6a was not that expected from the assumption of equal rate constants for 2, 5 and 6a. (Similar evidence has been obtained by S.J. Price (Thesis, Edinburgh) against the occurrence of the reaction

\[ \text{CH}_3 + \text{C}_6\text{H}_5 \cdot \text{CH}_2 \rightarrow \text{CH}_3 \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_5 \]

in toluene carrier experiments). The importance of the reaction is, however, in doubt. Since all three reactions are unlikely to have activation energies the proportion of phenyl radicals lost by reaction 6a should be temperature independent (this assumes that reaction 3 is sufficiently rapid for the rates of production of phenyl and methyl radicals to be equal). If this is so then the final rate constants will be in error by the same factor which in the worst case is two. Thus the uncertainty arising from 6a can be allowed for by increasing the probable error in log A by +0.3.

The preliminary runs (95% TBHP) are listed in Table 3. It can be seen that the system was more complex than originally expected, significant quantities of hydrogen, carbon monoxide and methane being produced. In addition the runs were irreproducible and the yields of diphenyl were so low that either a chain or heterogeneous decomposition seemed to be occurring (fraction of homogeneous reaction = 0.1 - 0.3 at 565°C). During these runs analysis of the non-
condensable gas was carried out with a copper oxide furnace and the condensable gas was assumed to be entirely ethane. Analysis of the condensable gas, however, indicated that it contained higher hydrocarbons. The apparatus was therefore redesigned to the form previously described to allow the complete analysis of the gaseous products.

Runs were then carried out using 98.5% tert-butyl hydroperoxide, with complete analysis of the gaseous products. In addition to the above products, oxygen, isobutene, and lesser amounts of other hydrocarbons were detected. These runs are tabulated in Table 4 (to avoid confusion, Run N refers to Table 4 unless it is specifically stated that Table 3 is meant).

Since the yields of diphenyl were low and the methane produced was of the same order as the isobutene, (Runs 2 - 16) it was suspected that some of the tert-butyl hydroperoxide might be decomposed by reactions 8a and 9.

For such a system,

\[
\frac{k_{8a}}{k_5^{1/3}} = \frac{R_{CH_4}}{R_{C_2H_6}} \cdot \frac{1}{[TBHP]}
\]

The values of \(\frac{k_{8a}}{k_5^{1/3}}\) were calculated from this relation using the average concentration of tert-butyl hydroperoxide in view of the high percentage conversion. These are listed in Table 4 for the first fifteen runs. It can be
NOTES ON TABLE 3.

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Condensable Gas C.G.

[TBP] = Initial Concentration Tert-butyl Hydroperoxide

m. moles THP passed during run.

THP Dec. = Number m. moles THP decomposed.

% hom. = Fraction Homogeneous Decomposition.

% age. = Percentage THP recovered.

Runs 10, 11, 12, 13 were carried out with a toluene carrier.

TABLE 3.

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</table>

**Rate constants:**

The rate constants (in mol-1 sec-1) have been calculated for some of the runs (13). These calculations have been made using the Arrhenius equation:

\[ k = A e^{\frac{-E_a}{RT}} \]

where:

- \( k \) is the rate constant (mol-1 sec-1)
- \( A \) is the pre-exponential factor (mol-1 sec-1)
- \( E_a \) is the activation energy (kcal mol-1)
- \( R \) is the ideal gas constant (1.987 cal mol-1 deg-1)
- \( T \) is the temperature (K)

The rate constants have been used for the Arrhenius plots to determine the activation energy and the pre-exponential factor. The plots were constructed using the following equation:

\[ \ln k = \ln A - \frac{E_a}{RT} \]

The plots were linear, indicating that the reaction follows an Arrhenius behavior. The slope of the plots can be used to determine the activation energy, while the intercept with the y-axis can be used to determine the pre-exponential factor.

**Notes:**

- The runs marked with an asterisk were carried out in a packed reaction vessel.
- The runs marked with an asterisk were carried out in a packed reaction vessel.
- The runs marked with an asterisk were carried out in a packed reaction vessel.
\[ \begin{array}{cccccccc}
C_2H_6 & i-C_4H_8 & 2(C_6H_5)_2 & \phi_{age} & \phi_{hom} & k_{tot.} & k_{hom.} & \frac{1}{T} \times 10^3 \\
12.1 & 6.4 & 45 & 81.2 & 0.512 & 0.674 & 0.345 & 1.742 \\
6.3 & 2.5 & 23 & 81.9 & 0.575 & 0.619 & 0.356 & 1.739 \\
123 & 96 & 49 & 6.87 & 0.051 & 8.721 & 0.441 & 1.745 \\
123 & 81.4 & 49 & 15.7 & 0.049 & 6.76 & 0.33 & 1.739 \\
219 & 116 & 70 & 23.3 & 0.058 & 5.43 & 0.315 & 1.745 \\
144 & 79.5 & 230 & 61.3 & 0.344 & 2.34 & 0.803 & 1.675 \\
66 & 35.6 & 160 & 66.7 & 0.340 & 2.05 & 0.695 & 1.684 \\
100 & 48 & 216 & 62.3 & 0.319 & 2.34 & 0.744 & 1.675 \\
100 & 60.5 & 502 & 30.5 & 0.563 & 3.56 & 2.00 & 1.631 \\
140 & 78.1 & 450 & 31.3 & 0.635 & 3.45 & 2.19 & 1.631 \\
96 & 46.4 & 376 & 35.3 & 0.641 & 3.37 & 2.16 & 1.634 \\
79.6 & 22.3 & 187 & 46.3 & 0.628 & 2.52 & 1.58 & 1.639 \\
75.2 & 22.6 & 204 & 39.6 & 0.647 & 2.96 & 1.91 & 1.636 \\
87.7 & 32.6 & 265 & 38.5 & 0.698 & 3.07 & 2.11 & 1.637 \\
222 & 136 & 518 & 29.7 & 0.449 & 3.77 & 1.69 & 1.634 \\
52.4 & 12.3 & 190 & 41.8 & 1.0 & 2.80 & 2.80 & 1.637 \\
212 & 115 & 461 & 10.2 & 0.359 & 8.72 & 3.14 & 1.575 \\
177 & 64.2 & 464 & 16.2 & 0.516 & 7.45 & 3.84 & 1.572 \\
169 & 81.5 & 440 & 16.3 & 0.467 & 7.23 & 3.38 & 1.577 \\
166 & 42.9 & 644 & 20.5 & 0.704 & 7.90 & 5.56 & 1.572 \\
249 & 50.9 & 638 & 23.4 & 0.697 & 7.33 & 5.10 & 1.570 \\
116 & 18.2 & 215 & 2.51 & 0.633 & 12.8 & 8.12 & 1.546 \\
136 & 18.5 & 313 & 3.33 & 0.705 & 11.5 & 8.07 & 1.546 \\
151 & 27.1 & 412 & 1.54 & 0.707 & 13.6 & 9.68 & 1.543 \\
109 & 15 & 324 & 1.64 & 0.787 & 13.3 & 10.47 & 1.543 \\
415 & 103 & 1,030 & 2.32 & 0.733 & 12.9 & 9.46 & 1.538 \\
298 & 62.2 & 836 & 1.81 & 0.743 & 14.0 & 10.4 & 1.539 \\
110 & - & 11.7 & - & - & - & - & - \\
\end{array} \]
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Note: DTBP represents another unit or measurement.
seen that the values are abnormally high for this temperature, the value for toluene being 42 litre$^3$ mole$^{-3}$ sec$^{-1}$ (S.J. Price, Thesis) and also they vary with tert-butyl hydroperoxide concentration. Further Figure 5 (Runs 27-48) shows that the methane was produced by a first order process.

For reactions 1, 2, 3, 4, 5, 8a and 9,

$$R_{CH_4} = k_8a [CH_3][TBHP]$$

$$R_{CH_4} = \frac{(k_8a [TBHP])^2}{2k_5} \pm \frac{k_8a [TBHP]}{2k_5} \sqrt{(k_8a [TBHP])^2 + 4k_1k_5 [TBHP]}$$

Thus when $k_8a [TBHP] > 4k_1k_5 [TBHP]$

$$R_{CH_4} \propto [TBHP]^2$$

and when,

$$k_8a [TBHP] < 4k_1k_5 [TBHP]$$

$$R_{CH_4} \rightarrow [TBHP]^{\frac{3}{2}}$$

Thus under no conditions could such a scheme give first order production of methane.

This indicated that a heterogeneous reaction was responsible for the high rates of decomposition and the low yields of diphenyl. This was confirmed by experiments in which the reaction vessel was packed with glass tubing increasing the surface/volume ratio by a factor of 6.7.

Runs in this reaction vessel (Runs 49, 50, 51, 52, 53 and
showed a marked increase in the rate of decomposition and in all the gaseous products, with the exception of hydrogen. A very important result was the decrease in diphenyl showing that it was produced homogeneously.

Calculation of the first order rate homogeneous rate constants was carried out on the assumption that both the homogeneous and heterogeneous reactions are first order. The justification of this assumption has been left to an appendix at the end of this section.

Where first order homogeneous and heterogeneous processes occur simultaneously,

\[
\frac{d[TBHP]}{dt} = (\frac{d[TBHP]}{dt})_{het} + (\frac{d[TBHP]}{dt})_{hom}.
\]

i.e.

\[k_{tot} = k_{het} + k_{hom}.
\]

Where the fraction homogeneous reaction = \(\phi_{hom}\).

\[k_{hom} = \phi_{hom} \cdot k_{tot}.
\]

i.e.

\[k_{hom} = \frac{2.303}{t} \left\{ \log \left[ \frac{TBHP}{TBHP_{initial}} \right] \right\} \times \phi_{hom}.
\]

This equation was used to calculate the homogeneous rate constants.

**Corrections.**

The following corrections have to be applied in the calculation of the results.
(a) The initial concentration of tert-butyl hydroperoxide was found by measuring the loss from the container in m.moles and multiplying by 0.985 to obtain the true concentration. This assumes that the purity was 98.5% and that the vapour had the same composition as the liquid.

(b) The weight of diphenyl has to be corrected for the loss due to its vapour pressure. (c.f. Figure 2) True wt. diphenyl = 1.06 (wt. collected) This was done by adding log 1.06 (0.025) to the logs of the rate constants before plotting on the Arrhenius curve. It can be seen that this error is fairly insignificant.

(c) The diphenyl collected was found to have a purity of about 75%. This was estimated by determination of the melting point and application of the equation,

\[ \Delta T = \frac{RT^2}{L_f} \cdot n \]

where \( \Delta T \) = depression of melting point.

\( L_f \) = latent heat of fusion of diphenyl.

\( n \) = mole fraction of impurity.

The purity seemed to be constant, as far as can be judged from such a crude method of determination, so that again a correction can be applied by adjusting the log k's by log 0.75, i.e. subtracting 0.13. Again the error is
quite small when considered in this way. It is not certain, however, whether or not this correction should be applied. Two possibilities exist. The impurity may be completely foreign material (e.g. dissolved benzene) or it may arise from the reactions of phenyl radicals. In view of the ambiguity the correction was not applied but has been accounted for by increasing the lower limit of the error in \( \log A \) by 0.13.

**Method of Calculation.**

The calculation of a typical run is shown below.

**Run 35**

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<th>Substance</th>
<th>Weight (mg)</th>
<th>Mole (mm)</th>
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<td>TBHP</td>
<td>94.4</td>
<td>1.049</td>
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<tr>
<td>Benzene</td>
<td>4.562 g</td>
<td></td>
</tr>
<tr>
<td>TBHP recovered</td>
<td>29.2 mg</td>
<td>0.324 m mole</td>
</tr>
</tbody>
</table>

Furnace Temperature = 612°A

Total Pressure = 15.1 mm.

Time of Run = 570 sec.

Contact time = \[
\frac{570 \times 87.5 \times 78 \times 273 \times 15.1}{4.562 \times 760 \times 22.4 \times 612} \times 10^{-3}
\]

= 0.338 sec.

\[
k_{tot} = \frac{2.303}{0.338 \log \frac{1.049 \times 0.985}{0.324}}
\]

= 3.44 sec\(^{-1}\).

\[
k_{hom} = \frac{3.44}{1.049 \times 0.985 - 0.324}
\]

= 2.18 sec\(^{-1}\).
\[
\log k_{\text{hom}} = 0.3385 + 0.025 = 0.364
\]

\[
\frac{1}{T} = 1.634 \times 10^{-3}
\]

The rate constants obtained are listed in Table 4. Those runs which were regarded as reliable, Runs 27-61 excluding 49, 50, 51, 52, 53, 54 in the packed reaction vessel, have been used to calculate the activation energy and A factor of the homogeneous decomposition by Least Squares (59) treatment of the Arrhenius plot (Figure 6). Runs 60 and 61 were weighted 50% as the quantity of diphenyl produced in these runs was only of the order of 0.5 ± 1 mg. Thus they can not be regarded as reliable. The point representing the average of these results has not been plotted on Figure 6 as it would have necessitated reducing the scale considerably. Runs 49, 50, 51, 52, 53, 54, have been plotted to show their positions. It can be seen that a lower A and E would be obtained from these points indicating that the method of calculation does not completely eliminate the heterogeneous contribution. It might thus be argued that the values obtained represent lower limits.

The homogeneous first order rate constant obtained from Figure 6, is

\[
k = 10^{13.67 \pm 0.25} \exp \left( -\frac{37,800 \pm 700}{RT} \right) \text{ sec}^{-1}.
\]
FIGURE 6

Tert-butyl Hydroperoxide

1 Packed R.V.
where the errors are the probable errors.

**Least Squares Method.** (59)

\( \frac{1}{T} \) was taken as the independent variable \( x \) and \( \log k_{\text{hom}} \) as the dependent variable \( y \). The mean point \((\bar{x}, \bar{y})\) was assumed to lie on the best straight line through the points.

Where \( X = x - \bar{x} \) and \( Y = y - \bar{y} \) the gradient of this line
\[
m = \frac{\Sigma XY}{\Sigma X^2}
\]

The probable errors in the slope \( m \) and the \( y \) intercept \( c \) are then given by the formulae,
\[
P_m = 0.6745 \sqrt{\frac{\Sigma d^2}{(n - 2) \Sigma x^2}}
\]
\[
P_c = 0.6745 \sqrt{\frac{\Sigma d^2 \Sigma x^2}{(n - 2) n \Sigma x^2}}
\]
\[
\Sigma d^2 = \Sigma x^2 \left\{ \frac{\Sigma y^2}{\Sigma x^2} - \left( \frac{\Sigma XY}{\Sigma x^2} \right)^2 \right\}
\]

\( n = \text{number of observations.} \)

Allowing for the doubt concerning the purity of the diphenyl and the recombination of phenyl and methyl radicals, this becomes,

\[
k = 10^{13.7 \pm 0.6} \exp \left( -\frac{37,800 \pm 700}{RT} \right) \text{sec}^{-1}
\]

Thus the activation energy obtained is in good agreement
with that of Bell et al. while the A factors differ. This can clearly be seen on Figure 7 where the open points represent the present work (the groups of points have been averaged for clarity) and the full points the work of Bell et al. It can be seen that the rate constants for the 0-0 bond split differ by a factor of about five. In view of the widely different methods used and the difference in the temperature ranges this can be regarded as reasonable agreement. Bell's values are also significantly higher than the total rate constants obtained in the present work. This indicates that the chain contribution to the reaction was not completely eliminated by the method of calculation used by these workers.

During the work attempts were made to reduce the extent of the heterogeneous reaction by treatment of the reaction vessel surface. At the start the reaction vessel was coated with boric acid (c.f. the hydrogen peroxide experiments). Removal of this coating and washing with concentrated hydrogen peroxide did not affect the surface activity. Towards the end of the work a coating of araldite resin was tried (Runs 55-61) with little effect. It therefore seems that the heterogeneous decomposition of tert-butyl hydroperoxide is not very specific. This conclusion should, however, be treated with reserve as it is based on very slight evidence. A point of interest concerning the
heterogeneous reaction is the apparent aging of the surface as found for hydrogen peroxide. This is shown by comparison of the values of \( \phi_{\text{hom}} \) for the preliminary runs 16-30 (Table 3) with the later runs in Table 4 (42-48).

Some experiments were also carried out to determine the source of the isobutene produced. By pyrolysing tert-butyl alcohol under typical run conditions at 567°C it was shown that the isobutene could not arise by the pyrolysis of tert-butyl alcohol present as an impurity. At this temperature the tert-butyl alcohol was found to dehydrate to an extent of about 20% in 1.4 sec. It seems probable, however, that at higher temperatures some of the isobutene will be produced by dehydration of tert-butyl alcohol from the heterogeneous decomposition.

**Appendix**

Owing to the nature of the experimental method used and the irreproducibility of the results, it was found difficult to determine the overall order of the decomposition. Some indication can, however, be obtained from the following considerations.

Figure 8 shows a plot of the percentage tert-butyl hydroperoxide recovered at constant contact time against the initial concentration of tert-butyl hydroperoxide, for Runs 16-30 Table 3. (The number of m.mole tert-butyl hydroperoxide passed during the run has been used as an
Initial Concentration TBHP, m. moles

% TBHP Recovered

n = 1

n = 1.25

n = 2.

Initial Concentration TBHP, m. moles

% TBHP Recovered

n = 1

n = 1.25

n = 2.

Figure 8

Centroid
FIGURE 9

Tert-butyl Hydroperoxide.

\[
\log k_{\text{het.}} = \frac{1}{T} \times 10^3
\]

\(\square \) Packed R.V.
indication of the initial concentration.)

For a reaction of n the order,

\[(n-1)kt = \frac{1}{(a-x)^{n-1}} - \frac{1}{a^{n-1}}\]

where \(k\) = rate constant
\(a\) = initial concentration
\(a-x\) = final concentration
\(t\) = time of reaction

If \(X = \frac{a-x}{a}\) & \(Y = a\)

then \(\frac{1}{Y^{n-1}} \left( \frac{1}{X^{n-1}} - 1 \right) = kt(n-1)\)

This equation was used to plot the curves shown in Figure 8. The result is not conclusive but it appears that the order of the reaction lies between 1.25 and 1. These runs were carried out under conditions where the heterogeneous reaction contributed about 30% to the overall rate. The order measured should therefore be close to that of the heterogeneous component since the homogeneous reaction is unlikely to be other than first order under the present conditions. Further it would be expected that as the temperature is raised and the homogeneous reaction becomes predominant the homogeneous first order rate constants would be more reproducible. That this is true can be seen from Figure 6. Figure 9, an Arrhenius plot of the heterogeneous first order rate constants shows the marked effect of packing
the reaction vessel and the irreproducibility of the heterogeneous rate constants. The activation energy for the heterogeneous reaction is about 24 Kcals/mole although it will be appreciated that this is only a rough estimate.

4.4) **ISO-PROPYL HYDROPEROXIDE.**

**Preparation.**

Initial attempts to prepare isopropyl hydroperoxide by the oxygenation of isopropyl magnesium chloride (60) were unsuccessful. The substance was therefore prepared from isopropyl methane sulphonate by reaction with cold alkaline hydrogen peroxide. The experimental details are as follows.

**Preparation of Isopropyl Methane Sulphonate (61).**

\[
\text{CH}_3\cdot\text{SO}_2\cdot\text{Cl} + \text{C}_3\text{H}_7\text{OH} + \text{C}_6\text{H}_5\text{N} = \text{CH}_3\cdot\text{SO}_2\cdot\text{C}_3\text{H}_7 + \text{C}_6\text{H}_5\text{N} \cdot \text{HCl}.
\]

0.5 mole methane sulphonyl chloride was mixed with 0.5 mole isopropyl alcohol at \(-20^\circ\text{C}\). 1 mole dry pyridine was then added with stirring over 4 hours, care being taken to keep the mixture below \(5^\circ\text{C}\). The mixture was then hydrolysed with 250 ml. 10% hydrochloric acid and extracted with 200 ml. ether. This solution was washed, dried, the ether removed and vacuum distillation of the residue yielded 58 gm. isopropyl methane sulphonate b.p. 71-72\(^{\circ}\text{C}/3\) mm.

(Yield, 85%).
Preparation of Isopropyl Hydroperoxide.

\[
\text{CH}_3\cdot\text{SO}_3\cdot\text{C}_3\text{H}_7 + \text{H}_2\text{O}_2 = \text{CH}_3\cdot\text{SO}_3\cdot\text{H} + \text{C}_3\text{H}_7\text{OOH}
\]

10 gm. 50% aqueous potassium hydroxide was added to a chilled solution of 80 gm. hydrogen peroxide, 0.1 mole isopropyl methane sulphonate and 75 ml. methanol. The mixture was then allowed to stand for 20 hours at 25°C. The hydroperoxide was then isolated from the solution by alternate extractions with ether and potassium hydroxide solution. As isopropyl hydroperoxide is completely miscible with water a large number of small portions of ether were used. The ether was then removed at reduced pressure. (The best yields obtained from this preparation were of the order of 20%.)

Purification.

The quantities of isopropyl hydroperoxide obtained were too small for purification by low pressure fractionation to be practicable. In addition it was found that extensive decomposition occurred if distillation was attempted. The hydroperoxide was therefore purified by gas chromatography. (p. 41). It was found that decomposition occurred on the column with the result that the hydroperoxide fraction had a purity of only 81.2% as determined by titration. This result was supported by gas chromatographic analyses. It was assumed during the work that the hydroperoxide vapour also had this composition.
Scheme and Results.

The system is identical to tert-butyl hydroperoxide except with regard to the lifetime of the alkoxy radical formed. The activation energy for the decomposition of the isopropoxy radical is probably about 20 Kcals/mole (56). Assuming a normal A factor of $10^{13}$ for the decomposition this would give the radical a lifetime of about $10^{-5}$ sec. at 600°F. This is too short for it to play an important part in the kinetics of the system (see section 4.5). Thus only the reactions

$$\text{(CH}_3\text{)}_2\text{CHO} + \text{OH} \rightarrow \text{(CH}_3\text{)}_2\text{CHO} + \text{OH}$$

10

$$\text{(CH}_3\text{)}_2\text{CHO} \rightarrow \text{CH}_3 + \text{CH}_3\text{CHO}$$

11

and reactions 3, 4, 5 and 6a of the previous section need be considered.

The complete experimental results are listed in Table 5. The method of calculation of the rate constants was identical with that for tert-butyl hydroperoxide, the isopropyl hydroperoxide concentration being corrected by a factor of 0.812. No packing experiments were carried out on this hydroperoxide but it is obvious from the nature of the products (hydrogen, oxygen, carbon monoxide, methane, propane, propylene and small quantities of higher hydrocarbons) and from the low values of $\phi_{\text{hom}}$ that a surface reaction occurred. The values of $\phi_{\text{hom}}$ are much lower than for tert-butyl hydroperoxide indicating much readier
<table>
<thead>
<tr>
<th>Units</th>
<th>Temperature T °C</th>
<th>Pressure P mm. Hg</th>
<th>Contact Time t sec.</th>
</tr>
</thead>
<tbody>
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<td>Notes</td>
<td><img src="image-url" alt="Image" /></td>
<td><img src="image-url" alt="Image" /></td>
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</table>

<table>
<thead>
<tr>
<th>T</th>
<th>P</th>
<th>t</th>
<th>[DPRE]</th>
<th>H₂</th>
<th>O₂</th>
<th>CO</th>
<th>CH₄</th>
<th>C₂H₆</th>
<th>C₃H₈</th>
<th>(C₃H₆)₂</th>
<th>%age.</th>
<th>Number of m.mole, isopropyl hydroperoxide passed during run. (Corrected to a purity of 81.2%)</th>
<th>Percentage isopropyl hydroperoxide recovered.</th>
<th>Quantities of diphenyl listed are measured amounts and are uncorrected. 0.025 was added to all the values of log khom. before plotting the Arrhenius curve.</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>557</td>
<td>13.7</td>
<td>0.099</td>
<td>1.048</td>
<td>0.6</td>
<td>13.7</td>
<td>4.3</td>
<td>13</td>
<td>54.8</td>
<td>25.2</td>
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<td>0.901</td>
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<td>4.9</td>
<td>18</td>
<td>54.4</td>
<td>25.4</td>
<td>9.2</td>
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<tr>
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<td>1.082</td>
<td>6.7</td>
<td>11.2</td>
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<td>58.8</td>
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<td>1.070</td>
<td>20.7</td>
<td>1.6</td>
<td>148</td>
<td>96.9</td>
<td>212</td>
<td>73.1</td>
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<td>262</td>
<td>11.4</td>
<td>0.277</td>
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<td>609</td>
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<td>0.982</td>
<td>15.5</td>
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<td>1.283</td>
<td>19.7</td>
<td>1.8</td>
<td>154</td>
<td>74.8</td>
<td>232</td>
<td>71.9</td>
<td>44.6</td>
<td>262</td>
<td>29.2</td>
<td>0.356</td>
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<td>0.361</td>
<td>0.999</td>
<td>12.8</td>
<td>3.7</td>
<td>264</td>
<td>30.2</td>
<td>169</td>
<td>65.1</td>
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<td>273</td>
<td>31.3</td>
<td>0.435</td>
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<td>628</td>
<td>14.6</td>
<td>0.360</td>
<td>1.071</td>
<td>23.6</td>
<td>17.2</td>
<td>133</td>
<td>95.5</td>
<td>292</td>
<td>76.2</td>
<td>65</td>
<td>242</td>
<td>17.0</td>
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<td>644</td>
<td>14.4</td>
<td>0.381</td>
<td>1.008</td>
<td>39.7</td>
<td>15.8</td>
<td>190</td>
<td>90</td>
<td>398</td>
<td>81.3</td>
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<td>0.331</td>
<td>0.732</td>
<td>60.7</td>
<td>10.1</td>
<td>127</td>
<td>57.7</td>
<td>203</td>
<td>64.7</td>
<td>14.2</td>
<td>466</td>
<td>1.76</td>
<td>0.649</td>
</tr>
<tr>
<td>15</td>
<td>652</td>
<td>15.9</td>
<td>0.353</td>
<td>0.980</td>
<td>64.5</td>
<td>25.8</td>
<td>163</td>
<td>74.6</td>
<td>232</td>
<td>68.8</td>
<td>23</td>
<td>336</td>
<td>2.02</td>
<td>0.599</td>
</tr>
</tbody>
</table>
heterogeneous decomposition of the isopropyl compound.

The Arrhenius plot of the homogeneous rate constants is shown in Figure 10. The equation for the first order rate constant derived from this line by the Method of Least Squares is,

\[ k = 10^{14.5 \pm 0.3} \exp\left(\frac{-40,700 \pm 800}{RT}\right) \text{ sec}^{-1}. \]

In these experiments it was found that the diphenyl produced had a purity of about 85%. Allowing for this and for the uncertainty regarding the recombination of phenyl and methyl radicals, this becomes,

\[ k = 10^{14.5 \pm 0.4} \exp\left(\frac{-40,700 \pm 800}{RT}\right) \text{ sec}^{-1}. \]

The calculation of the rate constants was again carried out on the assumption that the overall order was one. Figure 11 shows a plot of the log \( k_{\text{net}} \) against \( \frac{1}{T} \). The plot is linear indicating an order of close to one. In addition the rate constants do not depend on the contact time (compare Runs 6, 7 and 10, 11) as would be expected if an incorrect order had been used in their calculation. Thus it is reasonable to assume that the order is sufficiently close to one for the method of calculation of the homogeneous rate constants to be valid. The Arrhenius plot for the heterogeneous rate constants leads to an activation energy of about 15 Kcals/mole,
FIGURE 10

Isopropyl Hydroperoxide.
FIGURE 11

Isopropyl Hydroperoxide

\[ \log k_{het.} \]

against \( \frac{1}{T} \times 10^3 \)
significantly lower than that for tert-butyl hydroperoxide. This is once more indicative of the more rapid heterogeneous decomposition of isopropyl hydroperoxide.

In addition to the uncertainties discussed in the section on tert-butyl hydroperoxide the general instability of isopropyl hydroperoxide must be taken into account. It was found that the hydroperoxide tended to decompose in the liquid phase when heated or allowed to stand for long periods. For this reason the series of runs was carried out in as short a time as possible. At the end of the work the purity of the hydroperoxide in the container was checked by titration and found to be 81.2%. This compared favourably with the value found for the original sample before degassing and distillation into the container (82.3%). It is interesting to note that a further estimation of the purity of the hydroperoxide in the container after it had been standing for two months gave a value of 53%.

4.5) ETHYL HYDROPEROXIDE.

Preparation.

Ethyl hydroperoxide was prepared by oxygenation of ethyl magnesium chloride (60).

Ethyl magnesium chloride was prepared in third molar quantity (21 g. ethyl chloride, 5 g. magnesium and 200 ml. ether) centrifuged, made up to about 500 ml. with dry ether
and slowly added (3 hours) under the surface of 200 ml. oxygen saturated ether at -76°C. After stirring for 15 min. the mixture was poured into 200 ml. 5N hydrochloric acid. The acid solution was then extracted repeatedly with ether (ethyl hydroperoxide is completely miscible with water), the ethereal solution dried and the ether removed under vacuum at room temperature. The yields obtained by this method were of the order of 15%.

**Purification.**

The hydroperoxide was purified by gas chromatography and volumetric analysis of the product indicated a purity of 78.8%. Once more distillation was found impracticable owing to the small amounts involved and the ready decomposition. Two attempts were made to fractionate ethyl hydroperoxide on a 3 ft. Fenske helix column. The fractions collected were analysed for hydroperoxide by gas chromatography and the following results obtained. The quantity of hydroperoxide used was about 4 g. and two fractions were collected, P = 30 mm.

<table>
<thead>
<tr>
<th>Fraction</th>
<th>boiling point</th>
<th>Purity</th>
</tr>
</thead>
<tbody>
<tr>
<td>A₁</td>
<td>up to 25°C</td>
<td>64%</td>
</tr>
<tr>
<td>B₁</td>
<td>25-36°C</td>
<td>72%</td>
</tr>
<tr>
<td>C₁</td>
<td>Residue</td>
<td>81%</td>
</tr>
</tbody>
</table>

This was regarded as unsatisfactory. The fractions were therefore combined and redistilled, the fractions again
being analysed.

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>A₂</td>
<td>up to 36°C</td>
<td>59%</td>
</tr>
<tr>
<td>B₂</td>
<td>36-38°C</td>
<td>69%</td>
</tr>
<tr>
<td>C₂</td>
<td>residue</td>
<td>95%</td>
</tr>
</tbody>
</table>

Since the residue was quite small (½ g.) and appeared to consist partly of water (non-analysable by gas chromatography) the overall result was a loss of hydroperoxide. However this result is of interest in that it indicates that fractionation of ethyl hydroperoxide does not achieve much improvement in purity. The vapour must thus have a very similar composition to the liquid. This provides some justification for the assumption made throughout this work that the composition of the vapour from the hydroperoxide container is the same as that of the liquid. The result is not unexpected in view of the similarity in the boiling points of the hydroperoxides and the corresponding alcohols (the most probable impurities).

**Scheme and Results.**

The system differs from the previous two only in the stability of the alkoxy radical formed. The activation energy for the decomposition of the ethoxy radical is probably 15-25 Kcals/mole (56), giving the radical a lifetime of about $10^{-4}$ sec. at 600°C. If reference is made to the calculation of the rate of recombination of methyl radicals from tert-butyl hydroperoxide, it will be seen that
the concentration of methyl radicals is about $10^{-11}$ mole cc.$^{-1}$ at 600°C. The lifetime of a radical may be defined by the expression,

$$\frac{\text{conc.}^n}{\text{d}(\text{conc.}^n)}$$

i.e., for CH$_3$

$$\frac{[\text{CH}_3]}{\text{d}[\text{CH}_3]/\text{dt}} = \frac{[\text{CH}_3]}{R \text{C}_2\text{H}_6}$$

Since $R_{\text{C}_2\text{H}_6}$ is about $10^{-8}$ mole cc.$^{-1}$ sec.$^{-1}$ the lifetime of the methyl radical is about $10^{-3}$ sec. It is fairly certain from the tert-butyl hydroperoxide experiments that this is too short for the radicals to react other than by recombination. It is unlikely, therefore, that the ethoxy radical will have time to react before decomposing. If this is the case then only reactions,

$$\text{CH}_3\text{CH}_2\text{OOH} \rightarrow \text{CH}_3\text{CH}_2\text{O} + \text{OH} \quad 12$$

$$\text{CH}_3\text{CH}_2\text{O} \rightarrow \text{CH}_3 + \text{HCHO} \quad 13$$

and reactions 3, 4, 5 and 6a of Section 4.3 need be considered.

The complete experimental results are listed in Table 6. The method of calculation was the same as for the previous work and the hydroperoxide concentration was corrected by a factor of 0.788. No packing experiments were carried out but it is once more apparent from the nature of the results that surface reaction occurred. The values of $\phi_{\text{hom}}$ are comparable with those for isopropyl hydroperoxide.
NOTES ON TABLE 6.

Units:

Temperature \( T \) °A
Pressure \( P \) mm. Hg.
Contact Time \( t \) sec.

\([\text{EHP}] = \) Number of m.moles ethyl hydroperoxide passed during run. (Corrected for purity of 78.8%).

\( \% \text{age.} = \) Percentage ethyl hydroperoxide recovered.

\( \text{H}_2, \, \text{O}_2, \, \text{CO}, \, \text{CH}_4, \, \text{C}_2\text{H}_6, \, \text{C}_3\text{H}_8, \, (\text{C}_6\text{H}_5)^2 \) in \( \mu \text{mole} \).

\( k_{\text{tot.}} \) and \( k_{\text{hom.}} \) in sec\(^{-1}\).

\( \phi_{\text{hom.}} = \) Fraction homogeneous reaction.

Quantities of diphenyl listed are measured amounts and are uncorrected. 0.025 was added to all the values of log \( k_{\text{hom.}} \) before plotting the Arrhenius curve.

\( k_{\text{hom.}} \) for Run 8 has not been calculated as in this run loss of diphenyl from the trap occurred and the value of \( \phi_{\text{hom.}} \) is in error.
The Arrhenius plot of the homogeneous rate constants is shown in Figure 12 and Least Squares treatment of this line gives

\[ k = 10^{13.4 \pm 0.3} \exp\left(\frac{-37,700 \pm 800}{RT}\right) \text{ sec}^{-1}. \]

Allowing for a diphenyl purity of 85% and for reaction 6a, this becomes

\[ k = 10^{13.4 \pm 0.6} \exp\left(\frac{-37,700 \pm 800}{RT}\right) \text{ sec}^{-1}. \]

The Arrhenius plot of the heterogeneous first order rate constants is shown in Figure 13 and leads to an activation energy of about 18 Kcals/mole. The plot is reasonably linear indicating an order close to one. Thus no serious error is likely to be incurred in the assumption that the overall order of reaction is one. The rate of heterogeneous decomposition of ethyl hydroperoxide can be seen to be similar to that of isopropyl hydroperoxide.

In addition to the sources of error previously considered (Section 4.3) an uncertainty exists in this work owing to the instability of ethyl hydroperoxide in the liquid phase. As for isopropyl hydroperoxide the runs were carried out in as short a time as possible. At the end of the work, however, it was found that the purity of the hydroperoxide, as determined by titration, had dropped to 61%. Gas chromatographic analysis of the hydroperoxide
FIGURE 12

Ethyl Hydroperoxide

log $k_{hom.}$

$\frac{1}{T} \times 10^3$
FIGURE 13

Ethyl Hydroperoxide
vapour indicated a purity of 80%. Thus the impurity present was involatile or did not pass through the column. The most likely impurity of this nature is water.

Consideration of the order in which the runs were carried out shows that, if the vapour of the hydroperoxide had varied continuously in composition throughout the work, a break in the Arrhenius plot for \( k_{\text{hom}} \) would be expected. This would occur at a value of 1.62 - 1.64 on the \( \frac{1}{T} \) scale (between Runs 1-9 and 10-14). Reference to Figure 12 shows that a slight change in slope can be detected. It is not certain if this is due to the effect described but a rough estimate of the possible error can be made. If the best lines through the groups of points above and below \( \frac{1}{T} = 1.63 \) are estimated the slopes are found to differ from the overall value by about 3% in both cases. This indicates a further uncertainty of \( \pm 3\% \) in the values of \( A \) and \( E \) for the homogeneous reaction.

4.6) NOTE ON GASEOUS PRODUCTS.

Reference to Tables 3, 4, 5 and 6 shows that for the three hydroperoxides gaseous products have been tabulated although they are not necessary to the calculation of the rate constants. They have been tabulated to place them on record and also since they are indicative of the complexity of the products. It is certain that many other major
products are present e.g. alcohols, aldehydes and ketones. Since none of these was estimated it is not appropriate to discuss the few products which were measured. It will be noted, however, that the majority of the products increased with temperature.
DISCUSSION

The previous chapter describes how a method was developed for the study of the thermal decompositions of alkyl hydroperoxides and applied to the determination of the Arrhenius parameters for ethyl, isopropyl and tert-butyl hydroperoxides. The values obtained were:

<table>
<thead>
<tr>
<th>Hydroperoxide</th>
<th>log A</th>
<th>E Kcals/mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tert-butyl</td>
<td>13.3 - 14.3</td>
<td>37.8</td>
</tr>
<tr>
<td>Isopropyl</td>
<td>14.1 - 15.1</td>
<td>40.7</td>
</tr>
<tr>
<td>Ethyl</td>
<td>13.0 - 14.0</td>
<td>37.7</td>
</tr>
</tbody>
</table>

The Discussion will deal with the significance of these results. The activation energies obtained have a bearing on the thermochemistry of the hydroperoxides. The role of these compounds in oxidation systems will be considered in the light of the rate constants obtained and in addition mention will be made of their possible use as sources of hydroxyl radicals. The final section deals with the magnitude of the A factors obtained in studies of peroxide and hydroperoxide decompositions. First, however, it is necessary to give consideration to the reaction of hydroxyl with benzene.

5.1) REACTION OF HYDROXYL WITH BENZENE.

The majority of the uncertainties involved in the work
have been dealt with in the Experimental section. Since, however, the rate of reaction of hydroxyl with benzene is such an important factor in the reaction scheme it is proposed to discuss it in more detail. It is apparent that the reaction will occur for every hydroxyl radical if alternative reactions are too slow to compete. Some idea of the efficiency of the process may therefore be gained by consideration of the rate of the competing reactions. As has previously been pointed out recombination of hydroxyl radicals may be excluded as it is a third order reaction and probably has an activation energy \((57) (33)\). Since recombination of methyl radicals appears to be in its third order region at pressures of a few mm. \((62) (63)\) it is almost certain that at 15 mm. combination of methyl with hydroxyl is third order. Also recombination of methyl radicals is unusually fast reducing even further the possibility of reaction of methyl with hydroxyl. The importance of recombination of phenyl with hydroxyl is difficult to assess since no information is available for recombination of phenyls and of phenyl with methyl. Consequently this reaction can not be excluded on theoretical grounds. It seems unlikely, however, as phenol was found to be absent from the reaction products. No reactions involving alkoxy radicals are likely to be important since these radicals are rather short-lived. Thus the only
possible reactions of hydroxyl radicals would appear to be hydrogen abstractions, from benzene or hydroperoxide.

The activation energies for hydrogen abstraction by hydroxyl from some aldehydes and hydrocarbons are known. They lie in the range 0-8 Kcals/mole (64, 65) and seem in general to be some 4 Kcals/mole lower than for the corresponding reaction of methyl radicals. This would lead to an activation energy of about 6 Kcals/mole for hydroxyl hydrogen abstraction from benzene. In view of the reactivity of the radical it is likely that the abstraction from the hydroperoxides would have a similar value. Thus the rates of hydrogen abstraction from benzene and the parent hydroperoxide would be expected to be proportional to the pressures of the two species present. If this is so then a maximum of 2% of the hydroperoxide could be decomposed in this way. However this error is reduced by the fact that the decomposition of the peroxy radical formed is likely to generate a hydroxyl, methoxy or hydroperoxyl radical.

\[
\begin{align*}
(CH_3)_3COO & \rightarrow (CH_3)_2C=CH_2 + HO_2 \\
(CH_3)_3COO & \rightarrow (CH_3)_2CO + CH_3O \\
(CH_3)_2CHOO & \rightarrow (CH_3)_2CO + OH \\
(CH_3)_2CHOO & \rightarrow CH_3CHO + CH_3O \\
CH_3CH_2OO & \rightarrow CH_3CHO + OH \\
CH_3CH_2OO & \rightarrow HCHO + CH_3O
\end{align*}
\]
The actual mode of decomposition of the peroxyl radicals is in doubt (66) but one of the above processes is likely. If the methoxy radical is fairly reactive, as is quite probable, then it will abstract hydrogen from benzene. Consequently the yield of diphenyl will be relatively unaffected and $\phi_{\text{hom.}}$ will drop only as a result of the increase in the hydroperoxide decomposed. Further the effect on $k_{\text{hom.}}$ will tend to cancel out as $k_{\text{tot.}}$ rises (c.f. $k_{\text{hom.}} = k_{\text{tot.}} \cdot \phi_{\text{hom.}}$). This is sufficient justification for neglecting effects due to abstraction of hydrogen from the hydroperoxide and thus the reaction of hydroxyl with benzene may be assumed to be complete without incurring any serious error.

5.2) GROUP ENERGY TERMS.

Where experimental data is not available a reasonable estimate of the heat of formation of a molecule or radical may be made by use of group energy terms. The underlying principle of the method is that each grouping may be assigned an energy term $\Delta H(g_i)$, the sum of these terms giving the heat of formation of a molecule as a whole.

i.e. $\Delta H_f (X) = \sum \Delta H(g_i)$

This procedure gives values which generally lie within 2-3 Kcals/mole of the experimental result. Gray, and Gray and Williams (12, 67, 68) have recently made efforts to
place the thermochemistry of the alkoxy, hydroxyl and hydroperoxyl radicals on a sound basis and have obtained a fairly self-consistent set of values for the heats of formation of the alkoxy radicals. They have also obtained values for the group energy terms necessary to the calculation of the heats of formation of many radicals and molecules. They do not, however, list a value of the group energy term for hydroperoxyl in a hydroperoxide. Attempts to measure the heats of combustion of the lower alkyl hydroperoxides have so far proved difficult with the result that only tert-butyl hydroperoxide is known with any accuracy \((12, 69)\). Thus it would be of value to determine the group energy term for \(0\)OH in a hydroperoxide. This can be done using the activation energies obtained in the present work and the heats of formation of the alkoxy and hydroxyl radicals listed by Gray and Gray and Williams.

<table>
<thead>
<tr>
<th>Radical</th>
<th>(\Delta H_f) Kcals/mole at 25°C</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{OH})</td>
<td>8.9</td>
<td>64</td>
</tr>
<tr>
<td>(\text{CH}_3\text{CH}_2\text{O})</td>
<td>-8.5</td>
<td>65</td>
</tr>
<tr>
<td>((\text{CH}_3)_2\text{CHO})</td>
<td>-15.0</td>
<td>65</td>
</tr>
<tr>
<td>((\text{CH}_3)_3\text{CO})</td>
<td>-25.0</td>
<td>12</td>
</tr>
</tbody>
</table>

The group energy terms for methyl, methylene, tert-CH and \(-\text{CH}_3\) are also required. Gray gives these as

<table>
<thead>
<tr>
<th>Group</th>
<th>(\Delta H(g)) Kcals/mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{CH}_3)</td>
<td>-10.1</td>
</tr>
</tbody>
</table>
Group \[ \Delta H_{(g)} \text{ Kcals/mole.} \]

-CH\textsuperscript{-2} \[ -5.0 \]
-CH\textsuperscript{-} \[ -1.1 \]
-C\textsuperscript{-} \[ 0.8 \]

Then

\[ \text{ROOH} \rightarrow \text{RO} + \text{OH} \quad \Delta H \]

\[ \Delta H = E_1 - E_{-1} \]
\& \[ E_{-1} = 0 \quad \text{(Assumed)} \]
\[ \Delta H = \Delta H_f(\text{OH}) + \Delta H_f(\text{RO}) - \Delta H_f(\text{ROOH}) \]

Tert-butyl hydroperoxide (TBHP)

\[ \Delta H_f(\text{TBHP}) = -25.0 + 8.9 - 37.8 \]
\[ = -53.9 \text{ Kcals/mole.} \]

\[ \Delta H(\text{OOH}) = -3\Delta H(\text{CH}_3) - \Delta H(\text{C}) + \Delta H_f(\text{TBHP}) \]
\[ = 3 \times 10.1 - 0.8 - 53.9 \]
\[ = -24.4 \text{ Kcals/mole.} \]

Isopropyl hydroperoxide

\[ \Delta H(\text{OOH}) = 2 \times 10.1 + 1.1 - 40.7 - 15.0 + 8.9 \]
\[ = -25.5 \text{ Kcals/mole.} \]

Ethyl hydroperoxide

\[ \Delta H(\text{OOH}) = 10.1 + 5.0 - 37.7 - 8.5 + 8.9 \]
\[ = -23.0 \text{ Kcals/mole.} \]

The values obtained are in good agreement and the average of \(-24.3\) Kcals/mole, may be taken as the best value of \(\Delta H(\text{OOH})\). The value of \(\Delta H_f(\text{TBHP})\) \((-53.8\) Kcals/mole\) derived from group energy terms using this value is in good
agreement with the experimental value of -52.3 Kcals/mole (12, 69).

5.3) **ROLE OF HYDROPEROXIDES IN OXIDATION.**

Studies of oxidation reactions both in solution and in the gas phase have occupied the attention of a great number of workers. Although oxidation in solution is now fairly well understood (79), the exact nature of the processes occurring in the gas phase remains obscure. Since the introduction by Semenoff (70) of the concept of degenerate chaining it has been established that, depending on the temperature, the gas phase oxidation of hydrocarbons occurs by one of two degenerate branch chain mechanisms. The transition region is characterised by cool flames and negative temperature coefficients. The nature of the chain branching intermediate in the low temperature region, 250-400°C is still in doubt. It has been suggested by Norrish that aldehydes are responsible (71, 72). There are, however, many investigators who believe that hydroperoxides fulfil the role (73, 74). While there is only scant evidence to show that hydroperoxides are normally present in oxidation reactions, under favourable conditions they may be produced in high yields by the oxidation of hydrocarbons. Thus, at low temperatures, the mercury photosensitised oxidations of methane, ethane (75) and propane (76) and the
hydrogen bromide catalysed oxidation of isobutane (77) have led to high yields of the respective hydroperoxides. The most direct evidence in favour of the hydroperoxide theory is the finding by Taylor (78) that, in the oxidation of isobutane, tert-butyl hydroperoxide is produced during the induction period and is destroyed, concurrent with the production of hydrogen peroxide, by the passage of a cool flame. Recently Carldige and Tipper (80) have demonstrated the production of heptyl hydroperoxide and dihydroperoxide by the oxidation of heptane at 270°C in a helium carrier flow system. Also it is well established that the oxidation of olefins in solution occurs by a hydroperoxide mechanism (79). The uncertainty as to the role of hydroperoxides in the gas phase, low temperature oxidation of hydrocarbons is discussed in a review by Tipper (66).

The results of the present work have a bearing on this subject. An analysis of the kinetics of the oxidation of ethane and propane by Knox (81) indicates that the degenerate chain branching agents have lifetimes at 318°C of about 110 sec. and 65 sec. respectively. These lifetimes may be compared with the lifetimes of the respective hydroperoxides; about 3.5 sec. for both. Thus if these hydroperoxides were responsible for the branching then the acceleration constants would be very much greater than the observed values. There remains the possibility, however, that methyl
hydroperoxide fulfills the role. It may be argued that this substance is likely to have an activation energy midway between that of the alkyl hydroperoxides and hydrogen peroxide i.e. about 44 Kcals/mole. If this were so, with an A factor of about $10^{14}$ sec.$^{-1}$, methyl hydroperoxide would have a lifetime of the correct order. On the other hand, the present studies have shown that the alkyl hydroperoxides are all similar in activation energy and rate of decomposition. In addition, the activation energies for di-tert-butyl peroxide and tert-butyl hydroperoxide are the same. This is strong evidence that the nature of the substituent alkyl groupings does not have a marked effect on the O-O bond strength. Thus methyl hydroperoxide might be expected to have an activation energy of 38-42 Kcals/mole. This question can be resolved only by experiment. The present method is unlikely to be satisfactory for a study of methyl hydroperoxide due to the possibility of partial hydrogen abstraction by methoxyl radicals. The toluene carrier method might, however, prove successful if methoxyl were sufficiently reactive to give 100% hydrogen abstraction.

5.4) HYDROPEROXIDES AS SOURCES OF HYDROXYL.

Since, of the hydroperoxides studied, tert-butyl is the most stable to heterogeneous decomposition and is readily available, it is likely that it would prove the most suitable
for use as a source of hydroxyl radicals. A preliminary study of the decomposition of tert-butyl hydroperoxide in the gas phase using a static system (Duncan and Knox) indicated that the hydroperoxide undergoes fairly rapid heterogeneous decomposition at 200°C. If this could be reduced, however, tert-butyl hydroperoxide might be a suitable thermal source of hydroxyl radicals at temperatures of 150-200°C (in static systems). Photolytic decomposition of the hydroperoxide would enable the temperature range to be extended to considerably lower temperatures until the rate of decomposition of the tert-butoxy radical became the limiting factor. Photolysis of tert-butyl hydroperoxide would necessitate the use of ultra-violet light of fairly short wavelength as the lower alkyl hydroperoxides do not absorb strongly until about 2500Å (83). Thus the use of tert-butyl hydroperoxide presents difficulties. However these are probably not insurmountable and in view of the lack of knowledge concerning the reactions of hydroxyl such experiments would be justified.

5.5) HIGH A FACTORS.

It can be shown from transition state theory (82) that the rate constant for a unimolecular reaction is,

\[ k = K_\phi \frac{k_T}{h} e^{\frac{E}{RT}} \]

Where \( K \) = transmission coeff.
\( \Delta S^* \) = entropy of activation.
\[ R = \text{gas constant.} \]
\[ k = \text{Boltzmann's constant.} \]
\[ T = \text{absolute temperature.} \]

For most reactions the transmission coefficient is taken to be one. In general \( \Delta S^* \) is small since it is assumed that for a unimolecular reaction the activated complex is very similar to the normal molecule, differing only in energy content. Thus the \( A \) factor for a 'normal' unimolecular reaction is of the order of \( 10^{-13} - 10^{-14} \) sec\(^{-1} \).

In a great many instances \( A \) factors of this magnitude have been found for unimolecular decompositions; and, with the possible exception of isopropyl hydroperoxide, the values obtained in the present work are 'normal'. Often, however, \( A \) factors are found which lie outside the normal range.

Low \( A \) factors can, in general, be attributed to the transmission coefficient falling below unity although a negative entropy of activation may be responsible. High \( A \) factors are caused by an unusually large entropy of activation. This effect can be large enough to explain the high \( A \) factors found for the decompositions of the dialkyl hydroperoxides (Table 1), and is ascribed to an increase in rotational entropy in passing from the normal molecule to an activated complex in which free rotation is possible. In view of the small moment of inertia of the OH grouping this effect cannot explain entirely the abnormally high \( A \) factor for the
decomposition of hydrogen peroxide. The normal value for a bimolecular reaction is the collision number of about $10^{11}$ litre mole$^{-1}$ sec$^{-1}$ (82) and thus hydrogen peroxide is $10^4$ high. Gill and Laidler (36) have discussed the high rate of decomposition of hydrogen peroxide and have shown that it is higher than the maximum rate allowed by Slater's theory. The rates can, however, be explained on the Hinshelwood-Kassel-Rice-Ramsperger theory which postulates interchange of energy between degrees of freedom.

5.6) SUMMARY AND CONCLUSION.

It has been shown that tert-butyl, isopropyl and ethyl hydroperoxides have very similar rates of decomposition. Further they decompose too rapidly for them to be the degenerate branching agents in the gas phase, low temperature oxidations of hydrocarbons. In conclusion some indication may be given as to what remains to be done. As previously stated a study of the decomposition of methyl hydroperoxide is of prime interest and this might be attempted using the toluene carrier method. In view of the possible errors in the present work, also of great value would be a re-examination of the hydroperoxides studied using a different method. It might be possible to study the decompositions in a static system if, as with hydrogen peroxide, the surface could be sufficiently deactivated. Preliminary
experiments in this direction have, however, so far proved unsuccessful. It would also be of interest to extend the study to higher hydroperoxides. It is possible that a hydroperoxide could be found having a low tendency to heterogeneous decomposition and which would decompose giving an unreactive organic radical. Such a substance would enable the hydroxyl radical reactions to be studied in detail. Thus much work remains to be done in this field. This thesis can only be regarded as an initial contribution to the subject.
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