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THESIS

Presented in candidature for the degree of

Doctor of Philosophy

of the University of Durham

- by -

Alan Robertson, B.Sc., A.R.I.C.

- entitled -

THE LIQUID PHASE OXIDATION OF HYDROCARBONS

Being an account of the work carried out
at the Science Laboratories, Durham University
(Durham Division) and the Dyson-Perrin
Laboratories, Oxford University during the
period 1945-7 under the direction of
W.A. Waters, M.A., Sc.D., Ph.D., F.R.I.C.

THE LIQUID PHASE OXIDATION OF HYDROCARBONS.

The results described constitute the subject matter of a paper published in the Transactions of the Faraday Society (April 1946), a paper read at a meeting of the Chemical Society, Burlington House, Piccadilly, London (21st November 1946), and other papers awaiting publication.

I. HISTORICAL INTRODUCTION.

Reactions involving the oxidation of hydrocarbons both in the liquid and vapour phase are of commercial as well as theoretical interest. Whether such interest is directed towards the prevention of oxidation, as in the rubber and oil industries, or the promotion of oxidation, as in the paint industry, a knowledge of the reaction mechanism is desirable. Many attempts have been made to elucidate the mechanism of such oxidation processes. Early work in this field by Bone(1) and his contemporaries was particularly concerned with oxidation in the vapour phase; in recent years, however, with the expansion of the petroleum industry, liquid phase oxidation has been receiving the attention of an increasing number of workers. The term "autoxidation" has been defined by Waters(2) as "describing oxidations which can be brought about by oxygen gas at normal temperatures without the intervention of a visible flame or an electric spark". Autoxidations, although of a complex character, do not involve the thermal disintegration processes met with in high temperature vapour phase reactions.

Many hydrocarbons, when subjected to low temperature liquid phase oxidation with oxygen gas exhibit common features of behaviour. The process of oxidation is, for example, usually very susceptible to catalytic promotion and inhibition, and is often sensitive to light. In many cases the oxidising hydrocarbon can bring about the induced oxidation of added substances, and is sometimes capable of promoting polymerisation. Oxidation reactions are often autocatalytic and undergo an induction period (varying from seconds to hours) prior to a steady rate of oxygen absorption being attained. The products of oxidation cover a wide range of compounds including peroxides, ketones, alcohols, aldehydes, acids, esters, and polymerised materials. Controversial theories have been advanced to explain the kinetics and products of autoxidation, but none satisfactorily explain all the observed experimental data.

Research on the autoxidation of hydrocarbons may be resolved into three inter-related problems:-

(1) The nature of the primary product.

(2) The nature and mode of formation of secondary products.

(3) The mechanism of the overall reaction as interpreted from the observed kinetic and chemical evidence.

Early workers on autoxidation were interested in the mode of oxygen attack rather than resultant products, and Schonbein(3), Clausius(4) and Van't Hoff(5) related oxygen activity to either special types of oxygen or atomic oxygen.

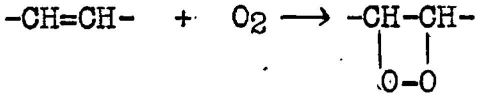
Hoppe-Seyler(6) suggested a reaction between oxygen and hydrocarbon of the type

$$X + O_2 \longrightarrow XO + O$$

with the possibility of a further reaction

$$Y + O \longrightarrow YO$$

if other acceptor molecules were present. In many cases, however, peroxides of the type XO_2 are formed and Bach(7) and Engler and Wild(8) advanced their "Peroxide" theory, which initiated a long controversy on the nature of the primary product. They postulated, as the first step in the oxidation process, the combination of the hydrocarbon and oxygen to form a peroxide or cyclic moloxide. They suggested that oxygen was absorbed molecule by molecule and added on at olefinic centres, the primary reaction being:-



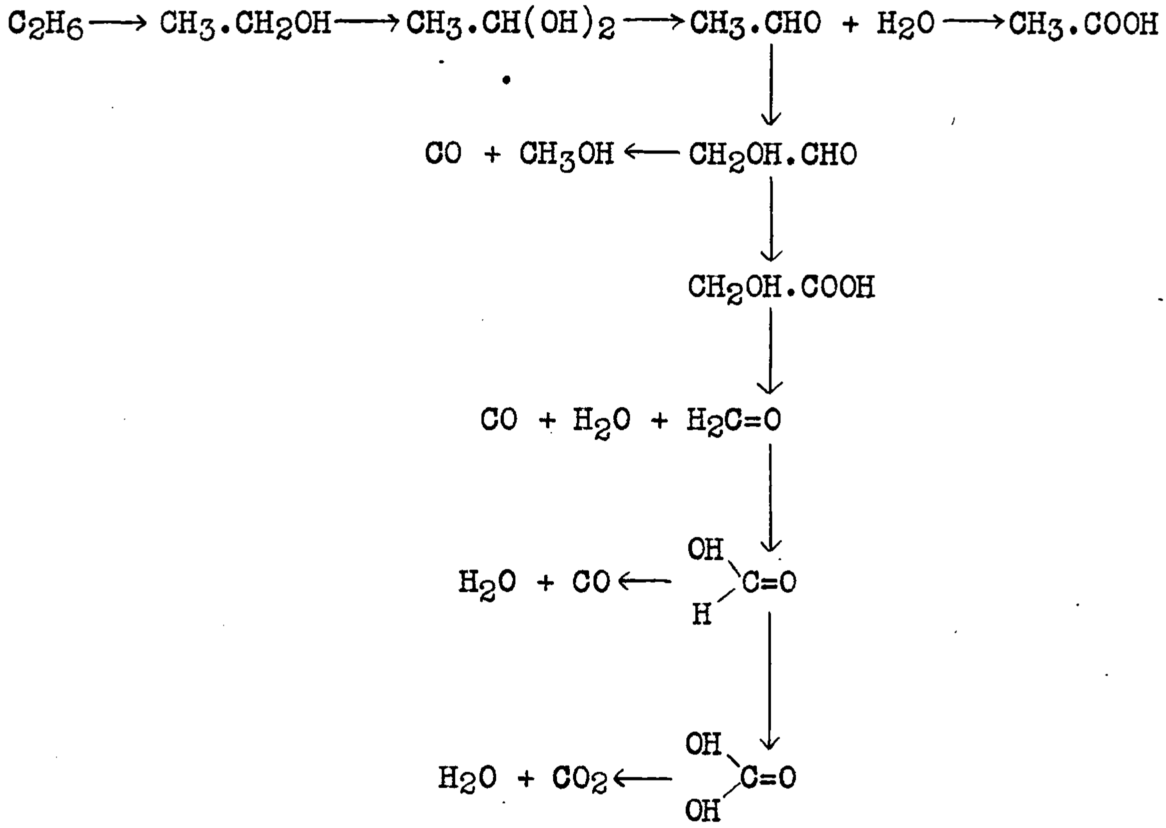
$$-CH{=}CH- \; + \; O_2 \longrightarrow \begin{array}{c} -CH-CH- \\ | \quad\; | \\ O-O \end{array}$$

In the presence of other acceptor molecules further reactions of the type

$$XO_2 + Y \longrightarrow XO + YO$$

might occur.

Many hydrocarbons, however, do not form peroxides which are capable of isolation, and often the rate of peroxide decomposition is so rapid that it prevents detection, especially in reactions carried out at high temperatures. Such difficulty in the detection of peroxides as primary products of oxidation resulted in alternative theories being put forward. H.E. Armstrong(9) in 1874 had suggested that the combustion of hydrocarbons involved the transient formation of hydroxylated molecules which then decomposed under the influence of heat. Bone and Wheeler(1) developed a similar theory and postulated that hydrocarbons did not initially undergo peroxidation, but that the oxidation mechanism involved a series of hydroxylations and thermal decompositions. Thus, according to Bone's "Hydroxylation" theory the oxidation of ethane could be represented by the following reaction scheme:-


$C_2H_6 \longrightarrow CH_3.CH_2OH \longrightarrow CH_3.CH(OH)_2 \longrightarrow CH_3.CHO + H_2O \longrightarrow CH_3.COOH$
$CO + CH_3OH \longleftarrow CH_2OH.CHO$
$CH_2OH.COOH$
$CO + H_2O + H_2C{=}O$
$H_2O + CO \longleftarrow$ OH, H, C=O
$H_2O + CO_2 \longleftarrow$ OH, OH, C=O

Bone(10) has summarised the evidence in favour of the "Hydroxylation" theory and pointed out that alcohols and aldehydes were identified as products of the slow combustion of almost all the hydrocarbons examined. Bone claimed that the only peroxidation observed was the secondary peroxidation of aldehydic products and suggested that other workers had confused this with primary peroxidation of the hydrocarbon.

Objections may be raised against the "Hydroxylation" theory. It does not, for example, give a satisfactory explanation of the observed kinetics of oxidation and a termolecular reaction of the type

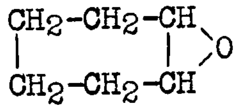
$$2CH_4 + O_2 \longrightarrow 2CH_3OH.$$

seems improbable. Furthermore alcohols which, according to the "Hydroxylation" theory, should be a primary product of oxidation, are rarely obtained in large quantities. It has been suggested that such difficulty in isolation probably arises from the fact that alcohols so formed undergo rapid oxidation, but much experimental evidence is available to refute this suggestion. Stephens(11) has shown that α phenyl carbinols when oxidised at 100°C. produced only very small yields of ketone. The chief products were high boiling compounds of an ether like character which he was unable to detect in the oxidation products of the parent hydrocarbon. Stephens also showed that using equimolecular amounts of ethyl benzene and phenyl methyl carbinol a much greater yield of acetophenone was obtained in a given time from the hydrocarbon than from the alcohol. Thus, the absence of an alcohol from the reaction products of the hydrocarbon could not be explained in this case on the basis of a rapid oxidation of the alcohol. The oxidation of xylene and ethyl benzene in the presence of acetic anhydride produced no esters of intermediate alcohols though the validity of conclusions from such experiments is doubtful because of the possibility that acetic anhydride may exert a directive effect on the reaction. Similarly Farmer and Sundralingham(12) found it impossible to oxidise cyclohexene-3-ol to the corresponding ketone and George(13) showed that alcohols were comparatively stable to low temperature oxidation and could not fulfil the role of a primary intermediate product.

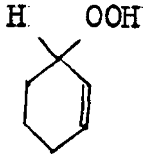
Bone's failure to detect large scale peroxide formation was probably due to the fact that he worked in temperature ranges at which peroxide decomposition would be extremely rapid. He was also unfortunate in his choice of titanic acid as a test reagent, for Egerton(14) has shown that it can only be regarded as of moderate efficiency for the detection of organic peroxides. Many other workers on the gaseous phase oxidation of hydrocarbons (Callendar(15), Egerton(16), Ubbelohde(17), Ivanov(18) and Mardles(19)) have obtained incontrovertible evidence of the formation of peroxides. In 1931 Rieche(20) summarised the properties and preparation of many organic peroxides and hydroperoxides, and shortly afterwards Hock and Susemihl(21) succeeded in isolating a crystalline hydroperoxide from a sample of oxidised tetralin.

The bulk of all recent evidence gives overwhelming support to the theory that peroxides are primary products of hydrocarbon oxidations. Hock and co-workers have isolated pure hydroperoxides from a number of hydrocarbons which had been subjected to low temperature oxidation. These included tetralin(21), cyclohexene(22), p.menthene(23), indan(24), ethyl benzene(25), p.xylene(25), octahydro anthracene(25), and cumene(26). Farmer and co-workers have obtained hydroperoxides from oxidised solutions of substituted cyclohexenes(27), methyl oleate(28), dihydromyrcene(29) and other polyisoprenes(30). In many of these oxidations a high percentage of the oxygen absorbed in the initial stages of the reaction was utilised in the formation of peroxides. Criegee, Pilz and Flygare(31) investigated the oxidation of olefinic substances and succeeded in isolating peroxides from cyclohexene, substituted cyclohexenes, and cyclopentene. Such evidence resolves the problem from a choice between the peroxide and hydroxylation theories to a detailed examination of the exact mechanism of the former.

Bach(7) and Engler(8) regarded the gradual decrease in the unsaturation of oxidising olefines as an indication of the addition of oxygen at the double bond, and Zelinski and Borissov(32) assumed that a compound they obtained by treating cyclohexene with oxygen at room temperature had a similar structure:-



Criegee, Pilz and Flygare(31), however, showed that the peroxide they obtained by treating cyclohexene with oxygen in ultraviolet light retained its unsaturation. They showed it to be a hydroperoxide with the structure



since it was reduced by sodium sulphite to cyclohexenol and would absorb one molecule of bromine per molecule. Farmer and Sundralingham(12) obtained confirmatory evidence of Criegee's work and it became evident that the simple Bach-Engler theory of addition of oxygen at the double bond required modification.

Moureu and Dufraisse(33) had demonstrated characteristic susceptibility of low temperature liquid phase oxidations to inhibition and advanced a theory of inhibitor action involving the induced oxidation of the inhibitor. They suggested that if A was an autoxidisable substance it would be capable of forming a primary peroxide $A(O_2)$ which would be an activated molecule. This primary peroxide would, under ordinary circumstances, eventually produce normal oxidised products

$$A(O_2) \longrightarrow AO_2$$

In the presence of an inhibitor B, however, the following reactions would take place preventing the development of the oxidation

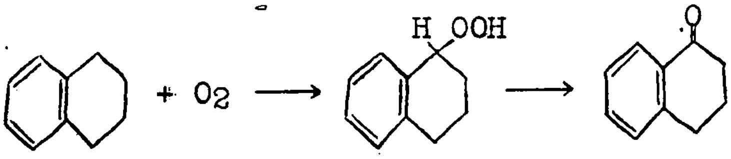
$$A(O_2) + B \longrightarrow A(O) + B(O)$$

$$A(O) + B(O) \longrightarrow A + B + O_2$$

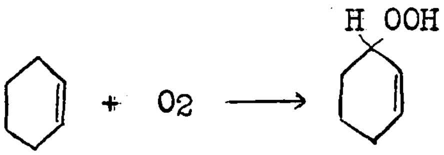
Christiansen(34) made the observation that the Moureu and Dufraisse theory failed to explain why such extremely small quantities of inhibitor were so effective, and suggested that inhibition of a reaction by small quantities of added substances could be regarded as a criterion of a chain mechanism. He advanced the theory that the function of an inhibitor was to prevent the formation or propagation of reaction chains. The efficacy of small quantities of inhibitors could then be explained, for if the reaction involved long chains, only a very small amount of inhibitor would be required to reduce the velocity of the reaction to a considerable degree by breaking chains soon after their initiation.

Bäckstrom(35) applied the Christiansen theory to the photochemical oxidations of benzaldehyde and enanthaldehyde, both of which are strongly susceptible to inhibition. He showed that the quantum efficiency of both reactions was so high that reaction chains were undoubtedly involved. The addition of small quantities of inhibitors reduced the quantum efficiency of the reaction and the inhibitors themselves underwent oxidation. It would be expected that inhibitors would undergo oxidation if they functioned by combination with chain carriers since the latter would probably be strong oxidising agents. The thermal oxidation of these aldehydes was inhibited in a similar manner and was presumed to possess a similar chain character. Chain reactions may be classified as "radical" or "energy" types depending upon the nature of the chain carriers. In the former case the chain carriers are free radicals, but in the latter they are molecules of product carrying an excess of energy (obtained during the reaction) which are able to activate molecules of reactant with which they come into contact. All autoxidations appear to fall into the general classification of chain reactions, though whether of the radical or energy type remains disputed. Waters(36) has pointed out that since molecular oxygen is paramagnetic and can be represented as a bi-radical containing two unpaired electrons it is possible that autoxidations are free radical addition processes.

Cook(37) and Criegee(31) both observed the fact that the activation of methylene groups by the proximity of double bonds was an important factor governing the susceptibility of a compound to oxygen attack. Cook showed that tetralin, when oxidised in the presence of metallic phthalocyanines, was attacked at the carbon atom adjacent to a double bond



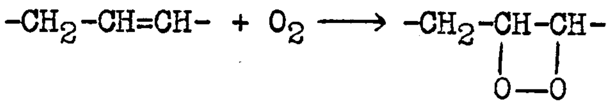
and Criegee proved that similar α methylenic attack occurred when cyclohexene was oxidised



Farmer(38) obtained further evidence of such activity from a series of researches on the oxidation of unsaturated substances and advanced a new theory of oxidation involving a radical chain mechanism to explain the observed α methylenic attack. He suggested that the primary step in the autoxidation of olefines of a non-conjugated structure was an attack on the methylene group adjacent to a double bond,

$$\mathrm{-CH_2-CH=CH-} + \mathrm{O_2} \longrightarrow \mathrm{-CH(OOH)-CH=CH-}$$

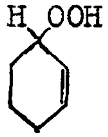
and not as postulated by the Bach-Engler theory at the double bond



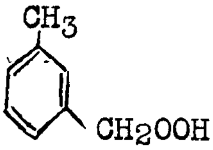
$$\mathrm{-CH_2-CH=CH-} + \mathrm{O_2} \longrightarrow \mathrm{-CH_2-}\underset{\mathrm{O{-}{-}O}}{\underset{|\quad\;\;|}{\mathrm{CH-CH}}}\mathrm{-}$$

In support of this theory various workers have shown that cyclohexene(12), substituted cyclohexenes(12), and tetralin(21) form hydroperoxides of type (1); m. and p.xylene(39) and cymene(40) form hydroperoxides of type (2); dihydromyrcene(29) forms a hydroperoxide of type (3); methyl oleate(28) forms hydroperoxides of types (4) and (5).

(1)



(2)



(3) $\mathrm{CH_2(OOH)-CMe=CH-CH_2-CH(OOH)-CMe=CH-CH_3}$

(4) $\mathrm{CH_3-(CH_2)_6-CH(OOH)-CH=CH-(CH_2)_7-COOMe}$

(5) $\mathrm{CH_3-(CH_2)_7-CH=CH-CH(OOH)-(CH_2)_6-COOMe}$

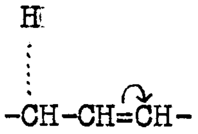
In all these cases the hydroperoxidic products retained the original double bonds intact except for small scale secondary reactions. Farmer pointed out that free radicals also attack olefinic substances in the α methylenic position and postulated as the main chain process an initial dehydrogenation to produce a radical which then combined with oxygen

$-CH_2-CH=CH- \longrightarrow -\underset{\bullet}{C}H-CH=CH-$,

$-\underset{\bullet}{C}H-CH=CH- + O_2 \longrightarrow \cdot O-O-\overset{|}{C}H-CH=CH-$,

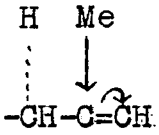
$\cdot O-O-\overset{|}{C}H-CH=CH- + -CH_2-CH=CH- \longrightarrow H-O-O-\overset{|}{C}H-CH=CH + -\underset{\bullet}{C}H-CH=CH-$

Evidence supporting such a free radical mechanism has been obtained by Ziegler(41 & 42) and co-workers who have shown that the free radical triphenylmethyl and other free substituted alkyl radicals can initiate the autoxidation of olefinic substances such as styrene, cyclohexadiene, and indene. The displacement of a methylenic hydrogen atom to produce the initial radical is facilitated in such unsaturated compounds by electronic displacements in the double bonded system which increase the tendency of the hydrogen to dissociate.



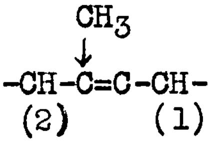
$-\overset{\overset{H}{\vdots}}{C}H-CH\overset{\frown}{=}CH-$

According to Farmer's theory, added effects would be superimposed by substituted groups attached to the ethylenic carbon atom adjacent to the methylenic group. Thus, an alkyl group would facilitate dissociation even further.



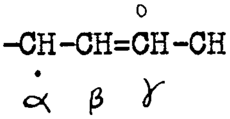
$-\overset{\overset{H}{\vdots}}{C}H-\overset{\overset{Me}{\downarrow}}{C}\overset{\frown}{=}CH$

If a compound contains a number of α methylenic centres, oxygen attack will take place at the point where the dissociation of hydrogen has been most facilitated by electronic polarisation effects. Thus attack will take place at C_2 in preference to C_1.



$$-\underset{(2)}{CH}-\overset{\overset{CH_3}{\downarrow}}{C}=C-\underset{(1)}{CH}-$$

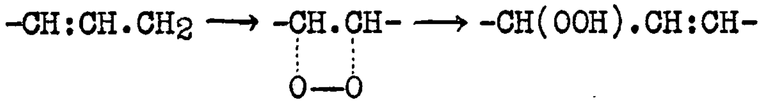
Olefines containing the $-CH_2-CH=CH-$ group are much more susceptible to oxidation than the saturated paraffins, probably because once the removal of the α methylenic hydrogen atom has been achieved the initial radical thus formed is resonance stabilised, the odd electron being retained by either the α or γ carbon atom.



$$-\underset{\alpha}{\underset{\cdot}{CH}}-\underset{\beta}{CH}=\underset{\gamma}{\overset{\circ}{CH}}-CH$$

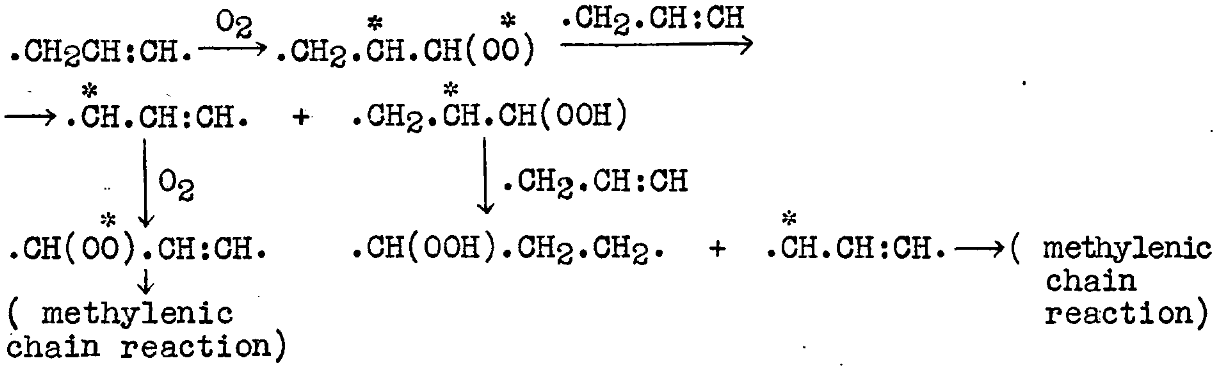
Such resonance stabilisation of the initial radical increases its mean free life and in consequence increases the probability of reaction with an oxygen molecule.

Morrell(43) and co-workers investigated the autoxidation of drying oils, but obtained results at variance with those of Farmer and rejected the theory of α methylenic attack in favour of attack at the double bond. Heinänen(44) also obtained results contrary to the Farmer theory and showed that methyl sorbate formed scission products which denoted the formation of a peroxide by oxygen addition at the γδ double bond. The two view-points may, to some extent, be reconciled by the work of Hilditch and Gunstone(45) who have shown that the point of oxygen attack may vary with temperature. They subjected methyl oleate to oxidation at temperatures varying from 20°C. to 120°C. and found that α methylenic attack prevailed at low temperatures, but as the temperature was increased an increasing proportion of ethenoid attack took place. Hilditch and Gunstone(46) suggested that the initial oxygen attack occurred at the double bond and not at the adjacent methylene group, hydroperoxide formation in the α methylenic position finally taking place with the formation of a new ethenoid bond.



$$\text{-CH:CH.CH}_2 \longrightarrow \text{-}\underset{\text{O—O}}{\text{CH.CH}}\text{-} \longrightarrow \text{-CH(OOH).CH:CH-}$$

From a consideration of the energy requirements of the initial reaction Farmer(47) has pointed out that there is justification for postulating initial attack by addition at the double bond and has modified his theory. Approximately 80 K.cals. of energy must be supplied if the detachment of an α methylenic hydrogen atom is regarded as the first step in the oxidation reaction, and Farmer suggested that such a high energy expenditure could be avoided if initial attack did occur at the double bond and thereafter at the α methylenic position by means of the following inter-molecular mechanism:-



$$
\begin{aligned}
&.CH_2CH{:}CH. \xrightarrow{O_2} .CH_2.\overset{*}{C}H.CH(\overset{*}{O}O) \xrightarrow{.CH_2.CH:CH} \\
&\longrightarrow .\overset{*}{C}H.CH{:}CH. \quad + \quad .CH_2.\overset{*}{C}H.CH(OOH) \\
&\qquad \Big\downarrow O_2 \qquad\qquad\qquad\qquad \Big\downarrow .CH_2.CH{:}CH \\
&.CH(\overset{*}{O}O).CH{:}CH. \qquad .CH(OOH).CH_2.CH_2. \quad + \quad .\overset{*}{C}H.CH{:}CH. \longrightarrow (\text{ methylenic chain reaction}) \\
&\qquad \downarrow \\
&(\text{ methylenic chain reaction})
\end{aligned}
$$

Addition at the double bond would be relatively small, but sufficient to initiate the necessary reaction chains to develop attack in the α methylenic position.

The oxidation of non-olefinic hydrocarbons generally proceeds less readily and intermediate products are more difficult to isolate than with unsaturated substances. The analysis of the final oxidation products does not always give a diagnostic indication of the original point of attack and in consequence the conclusions of different groups of workers often differ. Grün(48) concluded that oxygen tended to enter the carbon chain at a point removed as far as possible from a methyl group. Chavanne(49) and co-workers oxidised a series of hydrocarbons and obtained results indicating that oxygen attack occurred at the carbon atom of the methylene group adjacent to a terminal methyl group and not at the latter. Such conclusions agreed with those of Burwell(50) who suggested that oxygen did not attack paraffins at the terminal carbon atom but primarily at the β carbon atom, secondarily at the γ carbon atom, and thus progressively towards the centre of the molecule. Pope, Dykstra and Edgar(51) studied the oxidation of octanes and formed the opposite conclusion that oxygen attacked the molecule at the methyl group at the end of the longest carbon chain. Stephens(52) showed that alkyl benzenes with normal groups attached (e.g. ethyl benzene) were attacked at the α carbon atom, the hydrogen attached to the α carbon atom was removed and acetophenone was formed. Alkyl benzenes with secondary groups attached (e.g. isopropyl benzene) were also initially attacked in the α position, but when tertiary groups were attached (e.g. tertiary butyl benzene) no oxidation took place and Stephens concluded that for oxidation to take place at least one hydrogen atom should be attached to the α carbon atom.

Walsh(53) assumed a radical chain mechanism for the oxidation of saturated hydrocarbons and developed a theory governing the point of oxygen attack. Walsh pointed out that the order of reactivity of C-H bonds towards electrophillic reagents was $3^\circ > 2^\circ > 1^\circ$ and explained this graduation by:-

(1) The fact that this was also the order of decreasing amount of negative charge in CH bonds.

(2) The order $1^\circ > 2^\circ > 3^\circ$ was the order of decreasing bond strength.

Thus, assuming the oxidation of hydrocarbons involves free radicals as chain carriers, they would be expected to attack the hydrocarbon molecule (because of their electrophillic nature) at a tertiary carbon atom in preference to a secondary and at a secondary carbon atom in preference to a primary. Rice's(54) work on the thermal decomposition of hydrocarbons supports this theory. Rice found that at 300°C. the relative probabilities of attack by alkyl radicals at primary, secondary and tertiary carbon atoms were 1:3:33. Walsh concluded that the point of alkyl radical attack on hydrocarbons was governed primarily by the attraction of the radicals to, or their ease of reaction with local accumulations of negative charge, and whatever the nature of the radicals which attack hydrocarbons during their oxidation, the point of their attack would be governed by similar considerations. Since (as Stephens(52) has shown) a hydrogen atom is necessary for oxidation to occur at a particular carbon atom, Walsh suggested that the initial step in hydrocarbon oxidation was probably the removal of this hydrogen atom and the consequent formation of a hydrocarbon radical. The radical thus formed could then react with oxygen to form a peroxide by the following chain process:-

$$RH \longrightarrow R\cdot$$

$$R\cdot + O_2 \longrightarrow ROO\cdot$$

$$ROO\cdot + RH \longrightarrow ROOH + R\cdot$$

Such a chain process has frequently been suggested as the main sequence in the oxidation of both liquid and gaseous hydrocarbons(55, 56, 57).

Although there is strong evidence in favour of the theory that the first isolable products of hydrocarbon oxidations are peroxidic in character and that the mechanism of peroxide formation is of the general chain type shown above, little information is available about the chain termination reactions involved or the exact mode of the decomposition of the peroxides produced. George and Robertson(58) have suggested that metal catalysts present may function as chain terminators by reaction with peroxide radicals:-

$$RO_2\cdot + M \longrightarrow M \cdots RO_2$$

The same workers have also suggested that a chain termination reaction may occur between the chain carrier and oxygen molecules of the type:-

$$RO_2\cdot + O_2 \longrightarrow RO\cdot + O_3$$

It is doubtful whether such a reaction can be regarded as a chain termination since Briner, Demolis and Paillard(59) have shown ozone to be a catalyst of autoxidation, and it is difficult to imagine a reactive ozone molecule escaping reaction with vicinal hydrocarbon molecules. Sully(60) succeeded in isolating diphenyl butane from the oxidation products of ethyl benzene and suggested that the former resulted from interaction of two phenyl ethyl radicals. Such evidence supports chain termination by dimerisation of hydrocarbon radicals:-

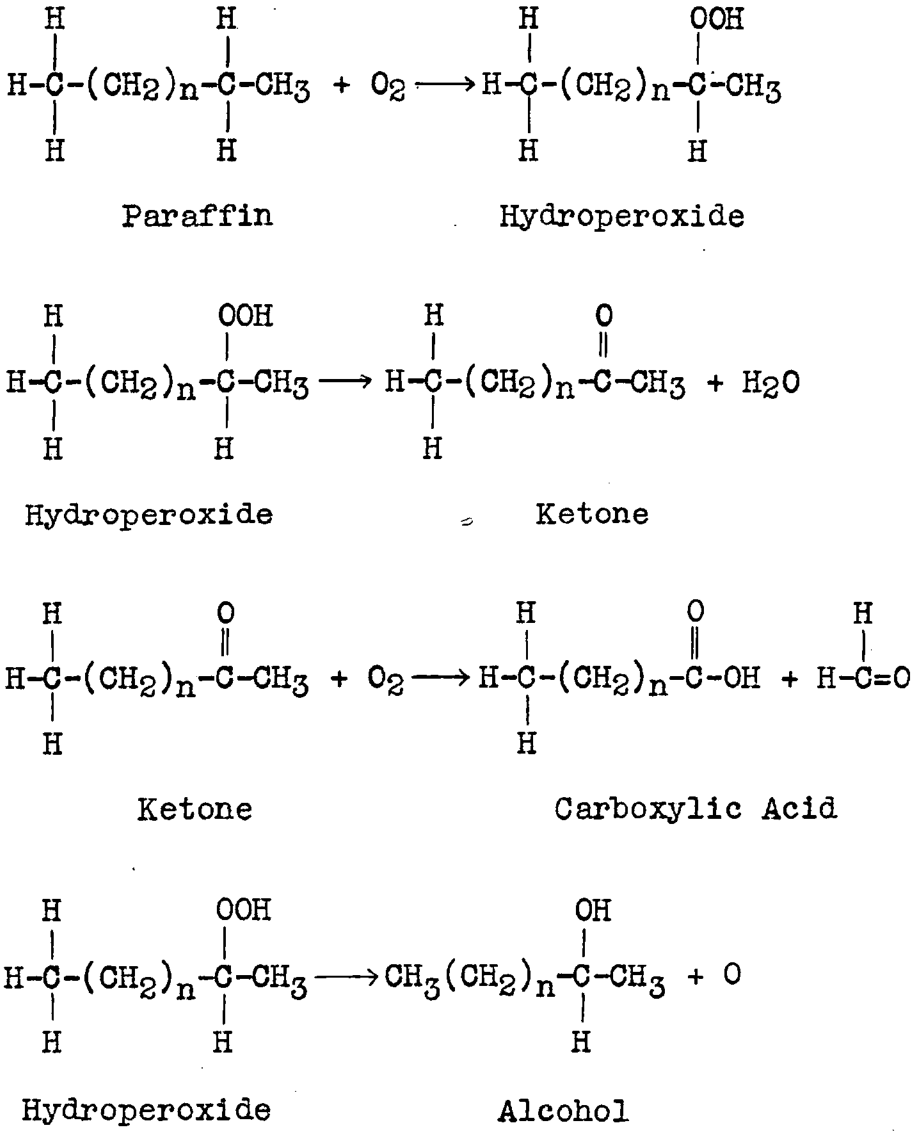
$$R\cdot + R\cdot \longrightarrow R\text{-}R$$

Bolland and Gee(61) believe that the usual termination reaction at normal pressures involves the interaction of ROO· radicals:-

$$2\mathrm{ROO}\cdot \longrightarrow \mathrm{R{-}OO{-}R} + \mathrm{O_2}$$

and they have obtained kinetic evidence from the autoxidation of ethyl linoleate supporting this theory.

The chief factor governing the nature of the secondary products of oxidation is the mode of decomposition of the intermediate peroxide. Zuidema(62) suggested that the products of the oxidation of paraffins could be accounted for by the following reaction scheme:-



$$\mathrm{H{-}\overset{H}{\underset{H}{C}}{-}(CH_2)_n{-}\overset{H}{\underset{H}{C}}{-}CH_3 + O_2 \longrightarrow H{-}\overset{H}{\underset{H}{C}}{-}(CH_2)_n{-}\overset{OOH}{\underset{H}{C}}{-}CH_3}$$

Paraffin Hydroperoxide

$$\mathrm{H{-}\overset{H}{\underset{H}{C}}{-}(CH_2)_n{-}\overset{OOH}{\underset{H}{C}}{-}CH_3 \longrightarrow H{-}\overset{H}{\underset{H}{C}}{-}(CH_2)_n{-}\overset{O}{\overset{\|}{C}}{-}CH_3 + H_2O}$$

Hydroperoxide Ketone

$$\mathrm{H{-}\overset{H}{\underset{H}{C}}{-}(CH_2)_n{-}\overset{O}{\overset{\|}{C}}{-}CH_3 + O_2 \longrightarrow H{-}\overset{H}{\underset{H}{C}}{-}(CH_2)_n{-}\overset{O}{\overset{\|}{C}}{-}OH + H{-}\overset{H}{C}{=}O}$$

Ketone Carboxylic Acid

$$\mathrm{H{-}\overset{H}{\underset{H}{C}}{-}(CH_2)_n{-}\overset{OOH}{\underset{H}{C}}{-}CH_3 \longrightarrow CH_3(CH_2)_n{-}\overset{OH}{\underset{H}{C}}{-}CH_3 + O}$$

Hydroperoxide Alcohol

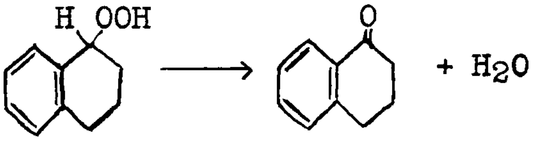
Zuidema suggested that esters could also be formed by the interaction of acidic and alcoholic products.

Whilst such a scheme involving molecular reactions and decompositions is attractive, available evidence suggests that products are often produced by a much more complex mechanism involving a chain fission reaction of the hydroperoxide. Harris(63) and Medvedev(64) have shown that primary alkyl peroxides undergo dehydration to an aldehyde. The decomposition is complex, however, and Medvedev reported that both unimolecular and bimolecular reactions took place in the case of methyl hydroperoxide:-

$$CH_3OOH \longrightarrow H_2O + HCHO$$

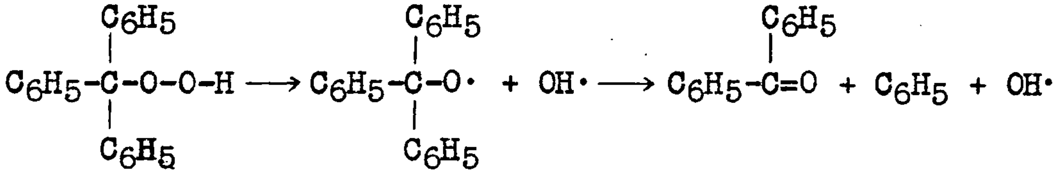
$$2\ CH_3OOH \longrightarrow 2\ CH_3OH + O_2$$

Secondary alkyl hydroperoxides often undergo dehydration to a ketone and Medvedev(55) has reported that this is the chief reaction in the decomposition of tetralin hydroperoxide:-



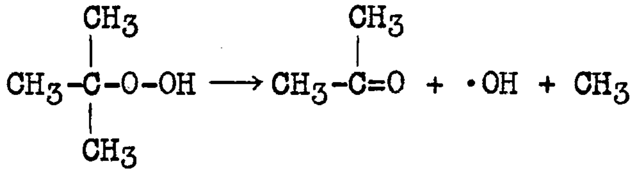
The reaction is more complex than denoted by this simple dehydration however, for Medvedev(65) has shown that the hydroperoxide is capable of initiating polymerisation.

George and Walsh(66) suggested that tertiary alkyl peroxides decompose by fission at the O-O bond and then by fission at the weakest adjacent bond of the ∝ carbon atom (other than the C-O bond). There is strong evidence supporting this theory: Wieland and Maier(67) showed that triphenyl methyl hydroperoxide decomposed to benzophenone and phenol which, according to the George and Walsh theory, could be regarded as occurring by the following steps:-



$$C_6H_5-\underset{\underset{C_6H_5}{|}}{\overset{\overset{C_6H_5}{|}}{C}}-O-O-H \longrightarrow C_6H_5-\underset{\underset{C_6H_5}{|}}{\overset{\overset{C_6H_5}{|}}{C}}-O\cdot \; + \; OH\cdot \longrightarrow C_6H_5-\overset{\overset{C_6H_5}{|}}{C}=O \; + \; C_6H_5 \; + \; OH\cdot$$

Similarly the decomposition of tertiary butyl hydroperoxide, which Milas(68) showed produced acetone and other products, including methyl alcohol, could be represented as:-



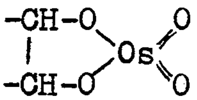
$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-O-OH \longrightarrow CH_3-\overset{\overset{CH_3}{|}}{C}=O \; + \; \cdot OH \; + \; CH_3$$

The decomposition of olefinic peroxides has been reviewed by Farmer(47) and by Paquot(69). It is even more complex than that of saturated hydroperoxides because of the higher probability of polymeric reactions, and as Farmer and Sundralingham(12) have shown interaction may occur between the hydroperoxide group and the carbon-carbon double bond to give epoxides.

Metal Catalysed Oxidation of Hydrocarbons.

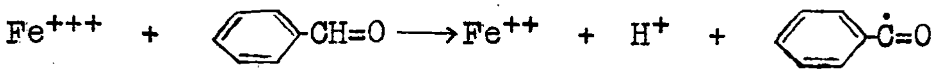
The oxidation of hydrocarbons is susceptible to catalysis by metals, particularly by compounds of metals which can readily undergo a valency change. It has been suggested by Stephens(70) that metal catalysts may function merely by destroying natural inhibitors present in the hydrocarbon. Bloomfield and Farmer(71) rejected this theory, and from their work on the catalysed oxidation of rubber preferred to regard metallic compounds as direct accelerators of oxidation rather than destroyers of inhibitors. Cook(72), who investigated the catalysed oxidation of benzaldehyde, and Davis and co-workers(73), who investigated the catalysed oxidation of lubricating oils, have shown that the metal catalyst concentration can reach a critical value above which the oxidation rate is independent of further increases in catalyst concentration. Similar results were obtained by Robinson(74) for the catalysed oxidation of linseed oil by haemoglobin and by George, Rideal and Robertson(13) for the heavy metal catalysed oxidation of tetralin. These latter suggested that such observations could be explained if the function of the metallic catalyst was both to initiate and terminate reaction chains. The facts that clean metallic surfaces can prevent peroxide formation in ether(75) and colloidal iron can inhibit the oxidation of benzaldehyde(76) support such a theory.

Wieland(77, 78) suggested that metallic catalysts functioned by complex formation, and it is possible that the oxidation of cyclohexene in the presence of metallic osmium investigated by Willstätter and Sonnenfeld(79) may function by such a mechanism since Criegee(80) has isolated osmic esters of the type:-



Manchot(81) has explained the catalytic properties of iron salts by the intermediate formation of peroxidic iron compounds, and evidence supporting this theory was obtained by Hale(82).

George, Rideal and Robertson(13) examined the catalytic properties of a large number of compounds for the oxidation of paraffinic hydrocarbons and obtained results suggesting that all good catalysts were ionic complexes. The rates of the catalysed oxidation of tetralin and paraffinic hydrocarbons were found to be proportional to the partial pressure of oxygen, which implied that the oxygen molecule was involved in the chain starting process and favoured complex formation. The same workers pointed out that the assumption that the varying catalytic activity of co-ordination compounds was due to the differing degrees of electrolytic dissociation was contrary to their physical properties and stereochemical behaviour. According to Wieland and Richter(83) catalysis of the autoxidation of benzaldehyde by traces of metallic cations could be accounted for by the production of a radical (which could then react with oxygen) by the following scheme:-



Other theories that catalytic activity is due to the heavy metal cation and involves valency change have been advanced. Waters(84), for example, pointed out that metallic catalysts for oxidation processes possibly function by electron transfer to the oxygen molecule to produce the anion of ·O-O-H (which could then initiate reaction chains):-

$$Fe^{++} + O_2 \longrightarrow Fe^{+++} + (\cdot O\text{-}O:)^-$$

The development of the "peroxide" theory of autoxidation and the actual isolation of hydroperoxides has helped to clarify the mechanism of catalysis by metals. The dependence of the kinetics of oxidation reactions upon the concentration of peroxide present in the system suggests that metallic catalysts probably function by promoting the formation and perhaps the decomposition of intermediate peroxides. According to Cook(37) iron phthalocyanine functioned as a catalyst for the oxidation of tetralin both by promoting the formation of tetralin hydroperoxide and by accelerating its decomposition to α tetralone. Ivanov, Savinova and Mikhailova(85) confirmed this theory by showing that heavy metal catalysts increased both the rates of formation and decomposition of the hydroperoxide. They found that the influence of catalysts on the rate of formation was more pronounced than on the rate of decomposition of the peroxide and presumed that the chief function of the catalyst was as an accelerator of peroxide formation. This dual function of metal catalysts has, in the past, led to the belief that the formation of hydroperoxides is hindered by their use (compare Plissoff(86)). This need not, of necessity, be the case because it is the balance of the formation-decomposition reaction rates which decides whether the formation or decomposition of the peroxide will be favoured.

There is a strong resemblance between metal catalysed oxidations and the metal catalysed decomposition of hydrogen peroxide, and it is possible that there is a similarity in the mechanism of these reactions. Haber and Willstätter(87) suggested that ferric salts decomposed hydrogen peroxide by the following mechanism:-

$$Fe^{+++} + H\text{-}O\text{-}O\text{-}H \longrightarrow Fe^{++} + H^{+} + \cdot O\text{-}O\text{-}H,$$

$$\cdot O\text{-}O\text{-}H + H\text{-}O\text{-}O\text{-}H \longrightarrow O_2 + H_2O + \cdot OH,$$

$$\text{or } (\cdot O\text{-}O:)^{-} + H\text{-}O\text{-}O\text{-}H \longrightarrow (\cdot O\text{-}O\cdot) + (H\text{-}O:)^{-} + (\cdot O\text{-}H),$$

$$\cdot O\text{-}H + H\text{-}O\text{-}O\text{-}H \longrightarrow H\text{-}O\text{-}H + \cdot O\text{-}O\text{-}H.$$

Haber and Weiss(88) later suggested that the free hydroxyl radical was first produced by the reaction:-

$$Fe^{++} + H\text{-}O\text{-}O\text{-}H \longrightarrow Fe^{+++} + H\text{-}O\cdot + (:O\text{-}H)^{-}$$

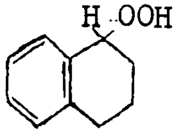
and was then followed by the sequence shown above. It is interesting that Haber and Weiss suggested that the catalyst could also act as a chain breaker by the reaction:-

$$Fe^{++} + \cdot O\text{-}H \longrightarrow Fe^{+++} + (:O\text{-}H)^{-}.$$

The Autoxidation of Tetralin.

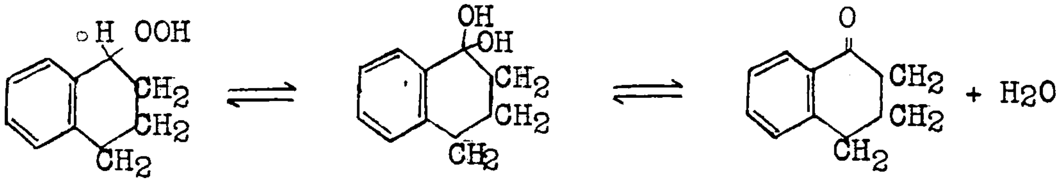
When investigating the mechanism of the oxidation of hydrocarbons in the liquid phase it is preferable that secondary reactions should be minimised, and this may best be achieved by the use of the lowest possible reaction temperature concomitant with a measurable rate of oxygen absorption. In order that a closer study may be made of the kinetics and decomposition products of the reaction, the compound selected for investigation should be capable of forming intermediate oxidation products which can be isolated. Tetrahydronaphthalene admirably fulfils both criteria: it oxidises at a measurable rate at 76°C. and forms an intermediate hydroperoxide which can be isolated as a pure crystalline compound.

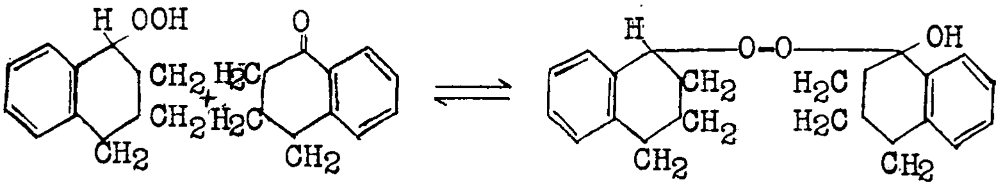
The tendency of tetralin to undergo atmospheric oxidation with consequent discolouration has been observed on several occasions(89, 90, 91), but no intermediate oxidation product was isolated until 1932. Hartmann and Seiberth(92), and a little later Hock and Susemihl(21), then succeeded in isolating a stable crystalline hydroperoxide. Oxidation of this hydroperoxide with potassium permanganate produced hydrocinnamic o.carboxylic acid, reduction with sodium bisulphite produced ac.tetrahydro ∝ naphthol, the action of warm sodium hydroperoxide produced ∝ tetralone, and thus the structure



was established.

Medvedev and Podyapolskaya(93) made a kinetic investigation of the autoxidation of tetralin and reaffirmed the Bach-Engler theory of a peroxide as the primary product and stated that all other products were formed as a result of peroxide decomposition. The mechanism of the oxidation, according to Medvedev and Podyapolskaya, could be resolved into two independent stationary chain reactions: one which was initiated by the thermal activation of the hydrocarbon and had a mechanism similar to that suggested by Bodenstein(94) for the gas phase oxidation of acetaldehyde and the other resulting from the decomposition of a peroxide complex formed by the collision of a tetralin hydroperoxide molecule with a molecule of α tetralone. Both reactions led to the accumulation of tetralin hydroperoxide in the system which gave the reaction its autocatalytic character. They suggested that the mode of decomposition of tetralin hydroperoxide could be compared with that of alkyl hydroperoxides, and using results obtained from the decomposition of methyl hydroperoxide, suggested that tetralin hydroperoxide could undergo the following reactions to produce a monohydroxy peroxide:-

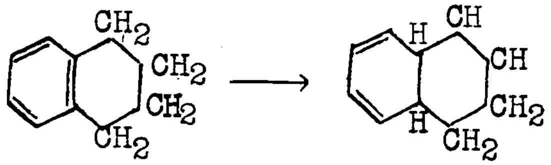




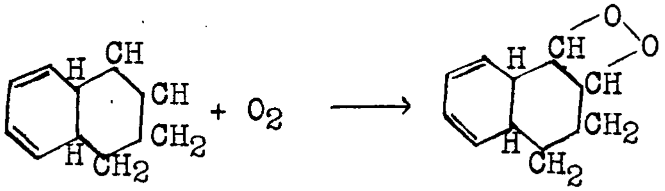
According to Medvedev the oxidation of tetralin occurred in the following stages:-

Process 1.

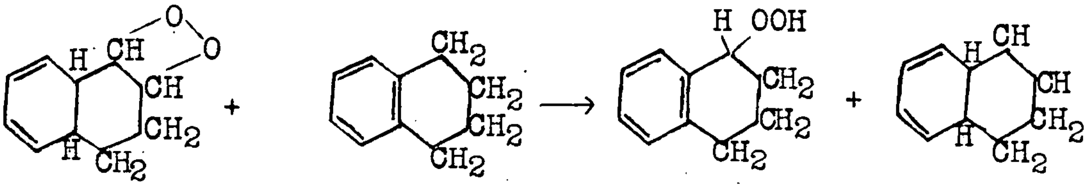
(a) Activation of the hydrocarbon



(b) Reaction of the activated hydrocarbon with oxygen

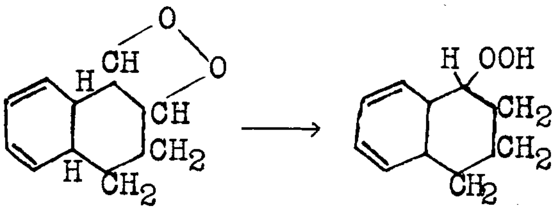


(c) Reaction of the activated peroxide with the hydrocarbon

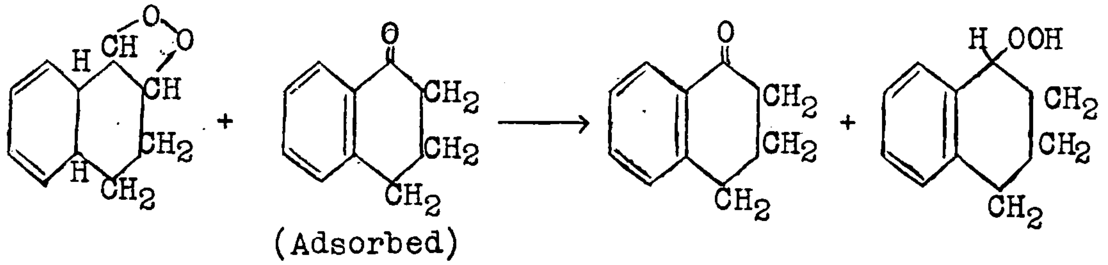


Chain Termination Reactions.

(d) Collision of the activated peroxide molecule with the wall.

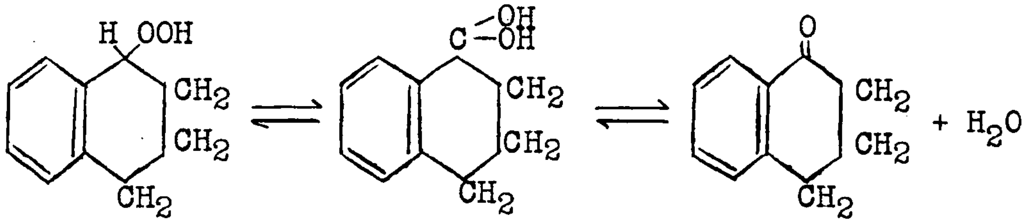


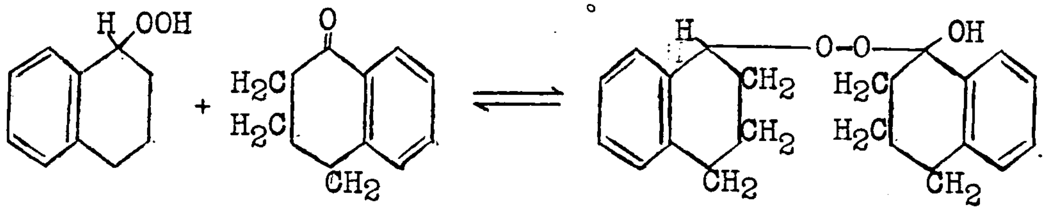
(e) Reaction of the activated peroxide with ∝ tetralone adsorbed on the wall.



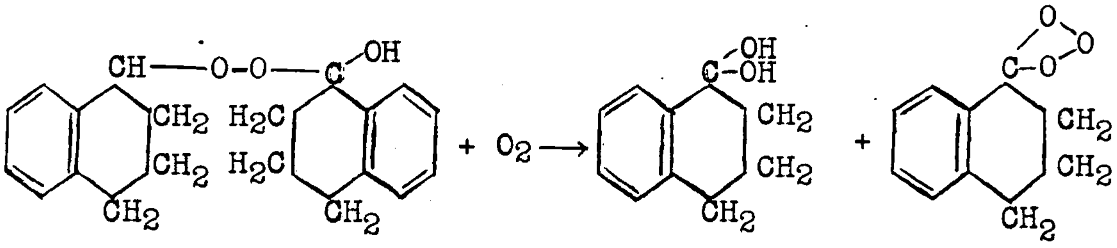
Process 2.

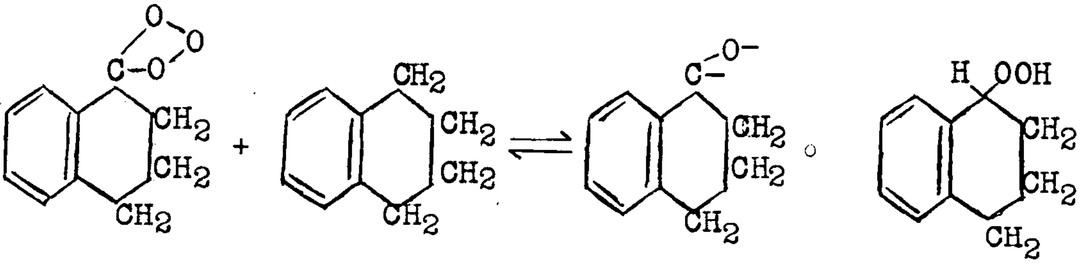
(a) Production of a monohydroxy peroxide.



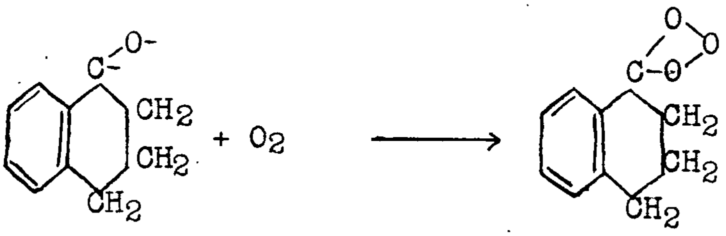


(b) Decomposition of the monohydroxy peroxide.

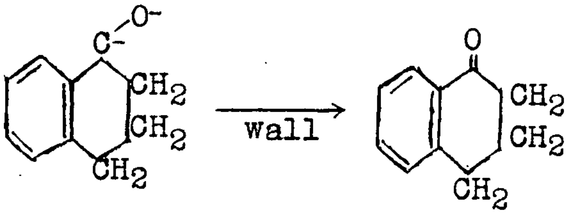


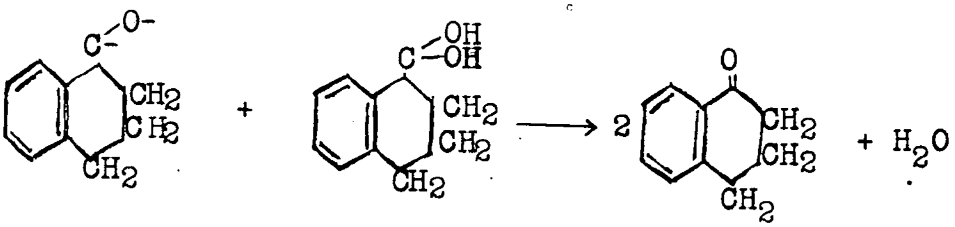


(b) Decomposition of the monohydroxy peroxide (Cont'd)

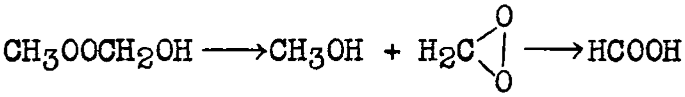


Chain Termination Reactions.



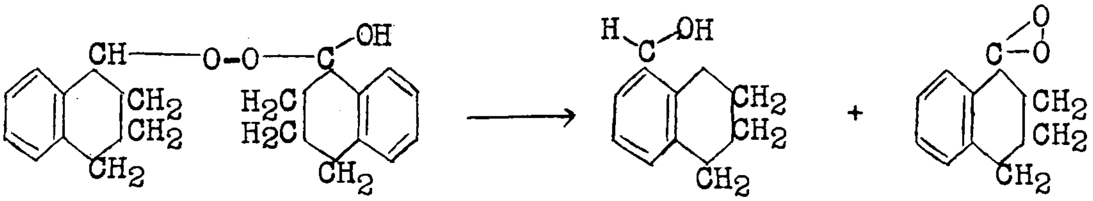


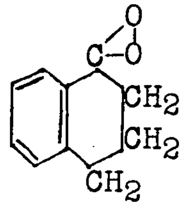
A secondary chain can arise from the decomposition of the monohydroxy peroxide which, according to Medvedev, is similar to that of monohydroxy dimethyl peroxide:-



$$CH_3OOCH_2OH \longrightarrow CH_3OH + H_2C\langle{}^{O}_{O} \longrightarrow HCOOH$$

thus,



with the difference that the compound  has greater stability because of its cyclic structure. This reaction rarely occurs, however, because of its high energy of activation.

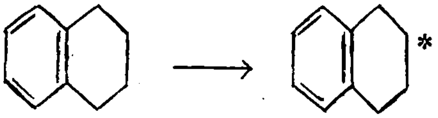
According to Medvedev, the velocity of the reaction could be represented by the expression:-

$$\frac{-d(O_2)}{dt} = a\frac{(A)^2}{1 + C_1\ (B_{ads.})} + b\ \frac{(P)(B_{ads.})(O_2)}{1 + C_2\ (B_{hyd.})}$$

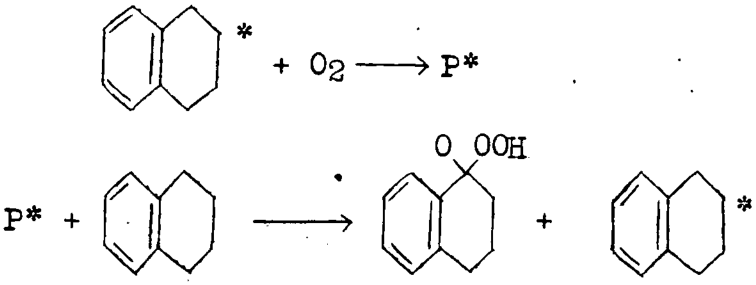
where A = tetralin, $B_{ads.}$ = adsorbed αtetralone, $B_{hyd.}$ = hydrated αtetralone and a, b, C_1 and C_2 are constants. Medvedev and Podyapolskaya found that αtetralone had an inhibitory effect on the oxidation and, contrary to George and Robertson's(95) findings, observed that the addition of tetralin hydroperoxide induced a marked increase in the rate of tetralin oxidation, thus confirming its role as a chain initiator. αTetralone was found to be the chief secondary product of the oxidation and Medvedev and Podyapolskaya were unable to detect the presence of alcoholic compounds. Failure to do so may have been related to the fact that the boiling points of αtetralol and αtetralone are identical and, in consequence, the αnaphthylurethane of αtetralol would probably be soluble in the excess of αtetralone present.

George and Robertson(95) have made an extensive investigation of the thermal, inhibited and catalysed oxidation of tetralin. They derived, by a development of the method of Alyea and Backstrom(96), expressions for the chain length of the oxidation and from a survey of their kinetic results concluded that the thermal oxidation had an energy chain mechanism of the following type:-

Chain initiation:-



Chain propagation:-

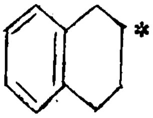


Chain termination:-

$P^* \longrightarrow$ inactive molecules

P^* + inhibitor $\longrightarrow$ inactive molecules

where P^* represents an energy rich peroxide molecule, and



represents an energy rich tetralin molecule.

George and Robertson found that the initial oxidation rate was independent of oxygen pressure and proportional to the square of hydrocarbon concentration. The addition of inhibitors did not alter the order of the reaction. Free radical mechanisms involving chain terminations by neutral reactions of alkyl or alkyl hydroperoxide radicals were rejected because they led to rate expressions which were proportional to fractional powers of both hydrocarbon and oxygen concentrations. Chain termination by interaction of alkyl and alkyl hydroperoxide radicals was also dismissed because this gave an expression for the reaction rate which was proportional to the first power of both hydrocarbon and oxygen concentrations.

According to George and Robertson, the rate of oxidation of tetralin at 108°C. was almost independent of the initial hydroperoxide concentration and they therefore concluded that the initiation and termination of primary chains could not be due to reactions involving the hydroperoxide molecule. Of a number of free radical mechanisms investigated, only one was compatible with identical orders for the inhibited and thermal rates, and this involved the formation of a hydrocarbon-oxygen complex capable of unimolecular decomposition to give a chain carrier. It was shown, however, that the initiation reaction was independent of the oxygen concentration, and it was concluded that the energy chain mechanism shown above best represented the thermal oxidation.

Metal Catalysed Oxidation of Tetralin.

George and Robertson(58) investigated the heavy metal catalysed oxidation of tetralin and concluded that the reaction had a free radical character. They suggested that the catalysed oxidation could be represented by the following mechanism:-

Chain initiation:-

$$M + O_2 \xrightarrow{K_1} M\text{------}O_2$$

$$M\text{------}O_2 + RH \longrightarrow M + R. + OOH.$$

Chain propagation:-

$$R. + O_2 \longrightarrow ROO.$$

$$ROO. + RH \xrightarrow{K_2} ROOH + R.$$

Chain termination:-

$$RO_2. + O_2 \xrightarrow{K_3} RO. + O_3$$

$$RO_2. + M \xrightarrow{K_4} M\text{------}RO_2.$$

Solution of the appropriate stationary state equations gave the following equation for the contribution of the heavy metal catalysis to the net oxidation rate.

$$\text{Rate} = \frac{K_1(M)(O_2)K_2(RH)}{K_3(O_2) + K_4(M)}$$

where M = metal catalyst, RH = hydrocarbon and K_1, K_2, K_3 and K_4 are reaction velocity constants. The oxidation rate was independent of the catalyst above a certain value, and it was suggested that the catalyst both started and terminated chains as shown above. The subsequent reaction was the unimolecular decomposition of the hydroperoxide via a heavy metal catalyst-hydroperoxide complex to give α tetralone. George, Rideal and Robertson(13) have shown that the catalysed decomposition of the hydroperoxide is a unimolecular reaction in which the reaction velocity constant is directly proportional to the catalyst concentration.

Both Medvedev and Podyapolskaya(93) and George and Robertson(95) based their theories on kinetic evidence alone and offered no chemical evidence for the various reactions they postulated. The kinetic evidence produced by the two groups of workers differs unfortunately on one of the fundamental factors of hydrocarbon oxidation - the role of the hydroperoxide. Medvedev and Podyapolskaya found the hydroperoxide to be an excellent catalyst for the oxidation whereas George and Robertson found it to have no marked effect. In view of this lack of chemical evidence and disagreement in kinetic results, it was decided to reinvestigate the mechanism of the liquid phase oxidation of hydrocarbons using tetralin (which, as already shown, is a suitable substance for this purpose) and to establish, if possible, a mechanism based upon both kinetic and chemical evidence.

THE LIQUID PHASE OXIDATION OF TETRALIN

II. STUDY OF OXYGEN ABSORPTION AND HYDROPEROXIDE FORMATION.

(a) Purification of Materials.

Autoxidation reactions are characterised by a strong susceptibility to catalysis and inhibition. In consequence, reproducible kinetic results can only be obtained if the hydrocarbon employed is free from all impurities.

Tetralin.

The tetralin employed in this research was supplied by Imperial Chemical Industries Ltd (Billingham Division), and it was prepared by the catalytic hydrogenation of naphthalene. The product was subjected to a rigorous purification by fractional distillation in a column equivalent to one-hundred theoretical plates. The product was finally redistilled in a stream of nitrogen and stored in dark vessels in an atmosphere of the same gas. Tetralin prepared in this manner had a peroxide content of less than 0.01%. An average batch had the following physical constants:-

Boiling Point (760 mms.)	207°C.
Refractive Index (n_D^{20})	1.541
Specific Gravity ($^{15}/_{15^\circ C.}$)	0.972

(These constants are in excellent agreement with those given in the literature(97).)

Analysis of the product for nickel and sulphur gave:-

Nickel	$< 0.0001\%$
Sulphur	$< 0.003\%$

Tetralin Hydroperoxide.

Methods listed in the literature describing the preparation of tetralin hydroperoxide (Hock and Susemihl(21), Hartmann and Seiberth(92), Nussle, Perkins and Toennies(98)) differ little in the technique employed. The three methods involved the thermal oxidation of the hydrocarbon at 70-75°C. by the use of air or oxygen for periods of approximately fifty hours. The hydroperoxide was then isolated by removing unoxidised tetralin and storing the concentrate at 0°C. or, alternatively, by treatment of the concentrate with strong sodium hydroxide and then isolating the sodium salt of the hydroperoxide thus formed.

On the basis of results obtained from kinetic experiments, a slight modification of the procedure of preparation was introduced. The methods described above employ an oxidation period of 50-60 hours: this may be considerably reduced by the use of a suitable quantity of cobalt naphthenate as a catalyst. The concentration of catalyst required to promote a maximum oxygen absorption concomitant with a minimum rate of hydroperoxide decomposition was obtained from results illustrated in Figure XXVII. Nussle and co-workers advocated the use of purified oxygen, but little difference could be observed when air was employed, and the use of the latter was adopted.

Tetralin containing 0.01% of cobalt naphthenate as catalyst was charged to a flask equipped with a reflux condenser and a glass frit gas distributor spoon (rubber connections were avoided because of the rapidity with which they were attacked by tetralin, thus causing crystallisation difficulties at a later stage of the preparation). The tetralin was air blown at a brisk rate and the temperature maintained at 75°C. for 25-30 hours. The product was then transferred to an all glass distillation apparatus and unoxidised tetralin removed by distillation at 1 mm. pressure (B.P. 52°C.) until approximately 20% of the original volume of tetralin remained. Tetralin hydroperoxide is relatively stable to thermal treatment at temperatures of less than 100°C., and there was little risk of explosion during the concentration process if normal precautions were observed. The hydroperoxide concentrate was stored at -10°C. overnight and the resultant crystalline product was separated by filtration through a sinter glass funnel. After pressing dry from the oily mother liquor, the hydroperoxide was purified by recrystallising three times from petroleum ether (40-60°C.) and then stored in vacuo over calcium chloride and protected from the light. The pure product melted at 56°C. Yield of crude product (calculated on original tetralin) = 17-20%.

Primary isolation by freezing was preferred to isolation as the sodium salt, because in the latter case highly coloured secondary products were often formed and were difficult to remove. The highly viscous nature of the hydroperoxide concentrate occasionally caused difficulties in crystallisation. Scratching with a glass rod, however, invariably promoted crystal formation and seeding was not found to be necessary.

(b) The Estimation of Tetralin Hydroperoxide.

The kinetics of an autoxidation can often be satisfactorily investigated by a periodic estimation of the peroxide content of the system. The accurate estimation of organic peroxides is unfortunately somewhat difficult, and many of the methods described in the literature, 'though giving excellent comparative results, are of little value for the purpose of an absolute determination of peroxide content. Engler and Weissberg(99) and Stephens(100) used stannous chloride for the estimation of amylene and cyclohexene peroxides, but could only obtain results which were 80% of their theoretical value. Yule and Wilson(101) estimated the peroxide content of gasoline by shaking a sample with ferrous sulphate and ammonium thiocyanate and then titrating the ferric salt which was formed with titanous chloride. Unfortunately in some cases (e.g. tetralin hydroperoxide) ferrous sulphate catalyses the decomposition of organic peroxides and results are not reliable. Klason(102) estimated the peroxides in turpentine by allowing the oil to stand for 24 hours in the presence of excess cymene hydrosulphide and then titrating the unused hydrosulphide with a solution of iodine. The reaction is very slow, however, and does not reach completion within 24 hours. Many workers, Wheeler(103), Lee(104), Hyman and Wagner(105), French(106), Marks and Morrell(107), Sharkey(108), and Risbey and Nisbet(109) have used variations of the method based upon the liberation of iodine from potassium iodide. None of these methods was entirely satisfactory for tetralin hydroperoxide 'though a further investigation of the iodimetric method appeared warranted.

Hock and Susemihl(21) reported that the reaction between tetralin hydroperoxide and potassium iodide was slow and even after long standing gave results which were only 85% of the theoretical value. Hock and Susemihl used glacial acetic acid as a solvent, and the variable blank titration obtained from the iodine liberated from solutions of potassium iodide in acetic acid when they are exposed to air, would be a factor which probably reduced the accuracy of their estimation. This variable was completely eliminated and the blank reduced until it was just detectable by starch reagent by:-

(1) Using pure acetic acid (Analar quality or triply distilled from chromium trioxide).

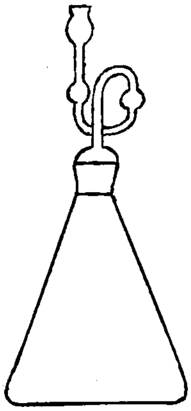
(2) Adding to the acetic acid used as solvent immediately before use 1.5 gm. solid sodium bicarbonate and a drop of water to ensure carbon dioxide evolution. The gas generated in situ adequately prevented the liberation of iodine from a potassium iodide-acetic acid mixture for periods up to twelve hours.

Effect of Catalysts on the Rate of Reaction.

Attempts were made to bring the reaction between the hydroperoxide and potassium iodide to a rapid completion by the use of ammonium molybdate and osmic acid as catalysts. Results obtained are shown in Table I. It can be seen that neither ammonium molybdate nor osmic acid offered advantages by their employment.

Effect of Heat.

Gentle heating of the mixture immediately after potassium iodide addition greatly increased the rate of reaction (see Table I) and excellent results were obtained when the liberated iodine was titrated after the sample had stood for a further one hour period. The extreme volatility of iodine necessitated stringent precautions during the period of heating and iodine loss by volatilisation was entirely eliminated by the use of a potassium iodide trap of the type shown in Figure I below:-



The following procedure was finally adopted.

Estimation by Volume.

A suitable quantity of the sample for analysis was withdrawn by a syringe pipette and transferred to a conical flask,fitted with a standard ground glass joint,containing 20 mls. glacial acetic acid, 1.5 gms. sodium bicarbonate, and sufficient water to bring about carbon dioxide evolution. (Quantities of water greater than a fraction of an ml. were avoided because larger quantities could exert an inhibitory effect on the reaction.) The pipette was rinsed with glacial acetic acid, the washings transferred to the flask, and the requisite quantity of a freshly prepared 50% potassium iodide solution added. The potassium iodide bubbler trap was then inserted, the flask heated at approximately 80°C. for fifteen minutes and finally stood in the dark for one hour. After standing, the potassium iodide solution from the trap was washed into the flask, the contents of the latter well diluted with water, and the liberated iodine titrated with decinormal sodium thiosulphate using starch indicator. During the final adjustment of the end point the mixture was well shaken prior to further additions because of the tendency of the iodine to separate into the tetralin layer.

Estimation by Weight.

In experiments where the oxidised product had become very viscous, it was found preferable to carry out hydroperoxide estimation using the following modification.

The sample was transferred by syringe pipette to a tared stoppered flask which had been purged with nitrogen to exclude the possibility of further oxidation of the sample. After re-weighing the flask and contents, a procedure identical to that outlined above was employed.

Accuracy of Method.

Analysis of pure tetralin hydroperoxide averaged 97% of the theoretical peroxide content over a series of estimations.

1 ml. $\frac{N}{10}$ sodium thiosulphate $\equiv$ 0.0082 gm. tetralin hydroperoxide.

Table I.

Analysis of Tetralin Hydroperoxide

Conditions	Percentage of Theoretical Value
Cold glacial acetic acid as solvent (24 hours standing)	85
Ammonium molybdate catalysed	88.5
Osmic acid catalysed	75
Heating and standing for one hour	97

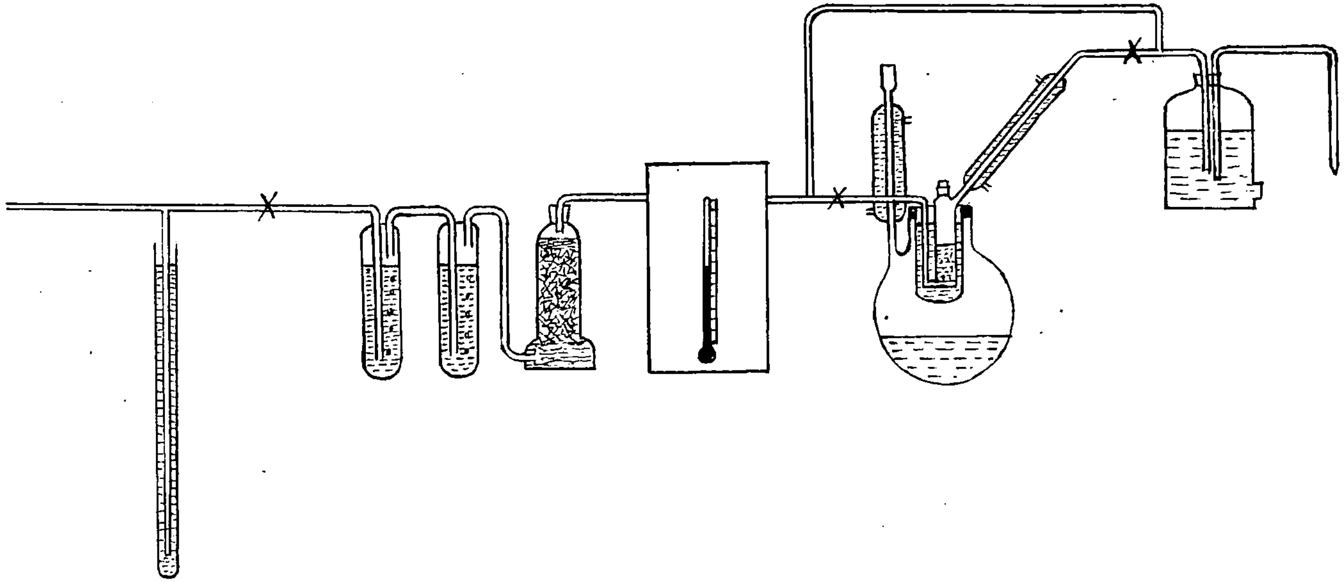
(c) Apparatus.

(i) Flow Method.

Preliminary experiments designed to investigate the rate of hydroperoxide formation during the oxidation of

Figure II.

Flow Apparatus



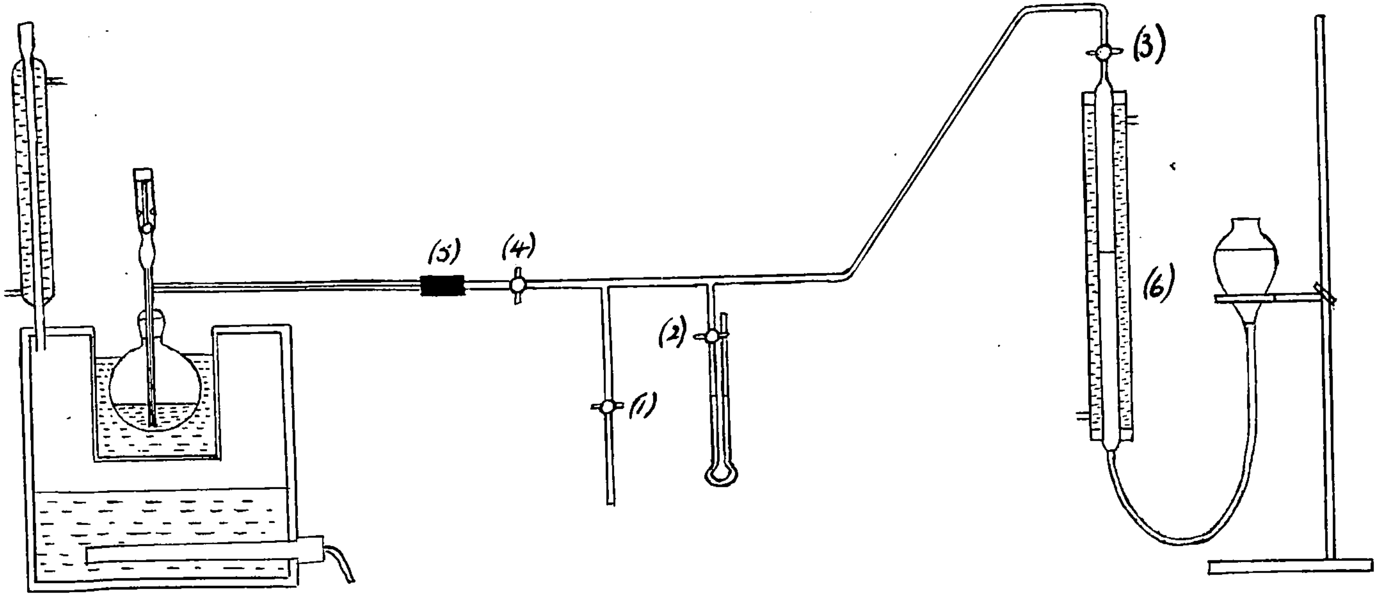
tetralin were carried out in the apparatus shown in Figure II. Cylinder oxygen (ex British Oxygen Company) was passed through a control tap via a safety lute into a purification chain of bubblers containing sulphuric acid and sodium hydroxide, and finally led through a calcium chloride tower before entering a flowmeter. The flowmeter was of the Pitot type and was calibrated to give accurate readings to within 0.2 ml./minute. From the flowmeter the oxygen entered the reaction vessel which was fitted with a sintered glass gas distributor spoon and a standard glass connecting joint to allow samples to be withdrawn during the course of the oxidation. Exit gases from the reaction vessel were led through a condenser to a Mariotte bottle in order to obtain an approximate estimate of their volume. A by-pass tube fitted on the reaction vessel side of the flowmeter allowed the apparatus to be purged and enabled samples to be taken without disturbing the gas flow rate. The reaction vessel was maintained at 76°C. by immersion in an oil bath heated by carbon tetrachloride vapour.

Procedure.

Thirty mls. of pure tetralin were transferred by pipette to the reaction vessel and the apparatus purged with a stream of nitrogen. As soon as a constant temperature was obtained, the apparatus was purged with oxygen via the by-pass tube. Finally, when the oxygen flow rate had been adjusted to 10 mls/minute, the gas stream was switched through the

Figure III.

Static Apparatus.



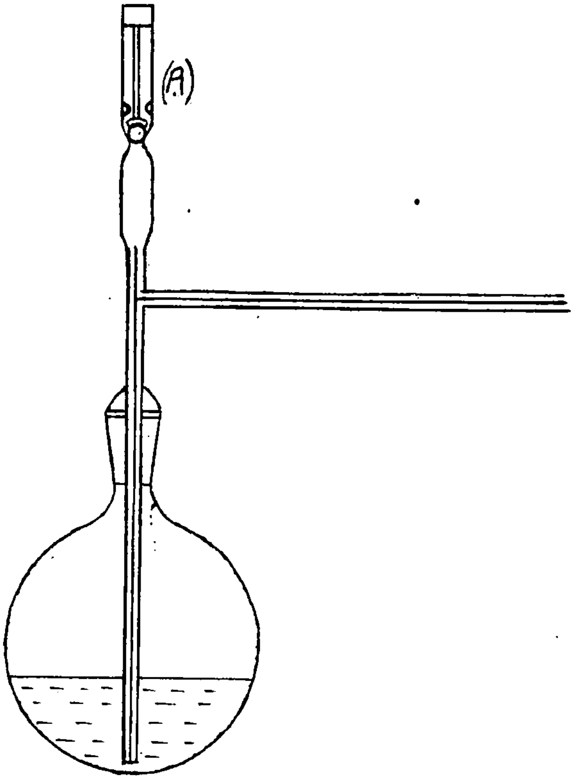
reaction vessel. The volume of exit gases was measured by collecting the water displaced from the Mariotte bottle during three minute periods measured by a stop watch. Samples were withdrawn at suitable intervals and the peroxide content estimated. This apparatus, 'though suited for the measurement of the rate of peroxide formation in the initial stages of the oxidation, had well defined limitations. The measurement of oxygen absorption was crude, and in advanced stages of oxidation when the oxidised hydrocarbon became viscous a back pressure was gradually built up in the apparatus, thus rendering flowmeter readings inaccurate.

(ii) Static Method.

The apparatus shown in Figure III was designed to enable a more accurate study to be made of the relation between the quantity of oxygen absorbed and the quantity of hydroperoxide formed, and to investigate the effect of the addition of selected substances both in the initial and intermediate stages of the oxidation. The reaction vessel was of the type shown in Figure III(a). It comprised a 100 ml. flask with a standard joint fitted with a device permitting the addition or withdrawal of substances without opening the system to the atmosphere. The valve device (designed for gas phase work by Dr. Gluckauf, University Laboratories, Durham) consisted of a grease-free stainless steel ball which fitted perfectly into the constricted portion of the

Figure III(a)

Reaction Vessel (Static Apparatus)



withdrawal tube 'A'. The seal between the ball and the glass wall was rendered completely gas-tight (tested at 12 mms. pressure) by previously grinding in an identical ball with carborundum power. A length of capillary tubing (bore approx. $\frac{1}{32}''$) was attached by an internal seal through a glass joint to the bottom of the withdrawal tube immediately below the ball valve, thus connecting the withdrawal tube with the reaction vessel. The capillary tube was just sufficiently long to reach the bottom of the reaction vessel when the latter was in place. A further constriction in the withdrawal tube immediately above the valve prevented ejection of the ball when a strong pressure was applied. Small lugs were attached to both the reaction flask and the male joint in order that strong rubber bands could be attached to keep the joint firmly inserted during agitation.

It can be seen from Figure III that when a positive pressure was applied to the reaction flask containing liquid, the latter was forced up the capillary tubing into the withdrawal tube lifting the ball valve in the process. As soon as sufficient solution for sampling had been lifted to the withdrawal tube, the pressure was removed and the ball valve dropped back into its seating making a perfect seal and isolating the sample in the upper part of the tube. After removing the requisite quantity of this sample by pipette the ball valve was lifted by external magnetic attraction and thus held until the remaining sample had drained back into the flask. The ball was then allowed to fall back into place, making a gas-tight seal once more. In this way samples could be withdrawn for analysis throughout the experiment without opening the system to atmosphere. A capillary side arm connected the main reaction vessel to a manometric system, the latter comprising an oxygen supply inlet, a butyl phthalate manometer and an oxygen reservoir calibrated to 0.1 ml. The butyl phthalate manometer was incorporated because of its sensitivity to small pressure changes, thus enabling readings to be observed with greater accuracy than could be achieved with the mercury manometer. For accurate gas measurement the oxygen reservoir was immersed in a water jacket to maintain it at constant temperature.

A tap system, Figure III (1, 2, 3, 4), enabled various parts of the apparatus to be isolated and allowed the oxygen supply to be replenished without interrupting the experiment. A small motor fitted with an eccentric cam was employed for shaking the reaction flask (3 oscillations/sec.) about the flexible rubber joint at (5). The agitation thus obtained was not of a limiting order, and increased agitation resulted in a slight increase of oxygen absorption. Measurements obtained, however, were not intended to represent absolute measurements of reaction velocity of the type made by George and Robertson and Medvedev and Podyapolskaya but to show as clearly as possible changes in the rate of oxygen absorption. The rate of oscillation was selected to give (with the volume of tetralin employed) a suitable rate of oxygen absorption, and since this rate was constant within narrow limits, comparative results could be obtained. The reaction flask was maintained at a constant temperature of 76°C. by immersion in an oil bath heated by carbon tetrachloride vapour. During rapid agitation the ball valve was held in place by a suitably shaped glass rod (see Figure III(a)).

Procedure.

Thirty mls. of tetralin were transferred, by pipette to the reaction flask, the glass rod adjusted to hold the ball valve in place, and the flexible joint at (5) coated with a cellulose acetate dope. The mercury reservoir was adjusted until all the air had been expelled from the calibrated tube (6), and the two-way tap (3) was closed. Tap (2) was then closed and the apparatus evacuated at the pump via tap (1). An oxygen supply was then connected to tap (1) and oxygen slowly led into the apparatus till atmospheric pressure was regained and the oxygen reservoir was filled. A slight positive pressure was applied and the apparatus tested for leaks. Finally tap (1) was closed and taps (2), (3) and (4) opened. The agitator was then started and the volume of oxygen in the reservoir observed after adjustment to atmospheric pressure using the butyl phthalate manometer. Thereafter oxygen uptake was periodically measured after adjustment to atmospheric pressure using the butyl phthalate manometer. Fifteen minute cycles were selected as an arbitrary unit of time for measurement of oxygen absorption since this, in the greater majority of experiments, gave suitable comparative values. The oxygen reservoir was replenished from time to time by closing tap (4) thus isolating the reaction flask, and then opening tap (1) to the oxygen supply.

The effect of the addition of selected compounds at different stages of the reaction was investigated by placing a weighed quantity of the compound under investigation in the withdrawal tube above the ball valve, and then washing it into the reaction vessel by applying pressure, by manipulation of the mercury reservoir, to raise and lower the tetralin level. During this process the ball valve was held open by external magnetic force. In order to obtain repeatable results, care had to be taken in cleaning the reaction flask and the following standard procedure was adopted:-

(1) Washing with alcohol,

(2) washing with chromic-sulphuric acid,

(3) washing with distilled water, and

(4) rinsing with alcohol and drying in a stream of hot air.

In later experiments investigating the effect of added compounds on the initial oxygen absorption rate, the ball valve was dispensed with and replaced by a small tap funnel.

Figure IV.

Barcroft Apparatus.

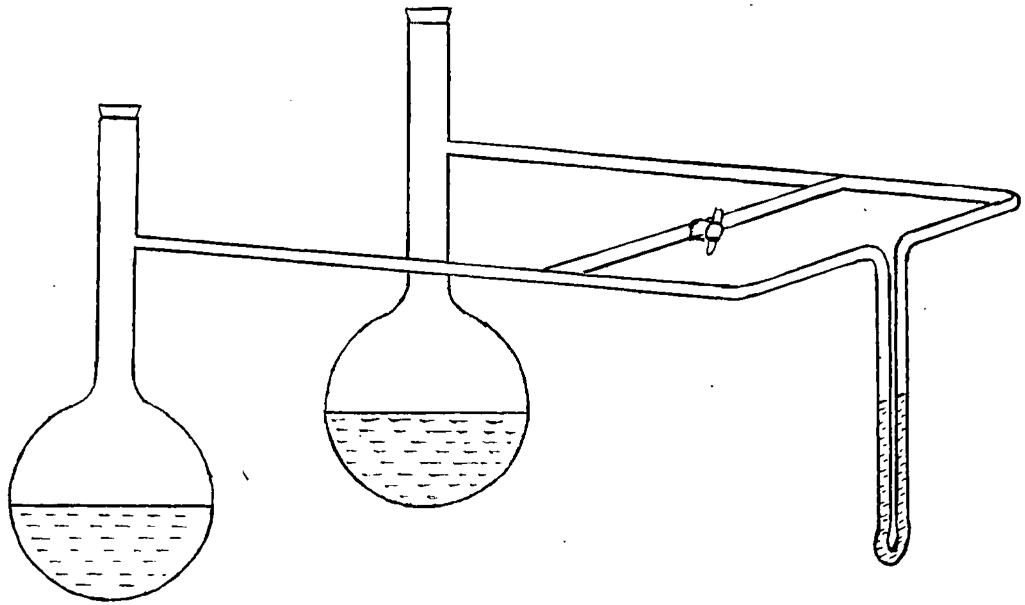


Table II demonstrates the reproducibility of results obtained with this apparatus.

Table II.

Oxidation of Tetralin in the Presence of Benzyl Chloride.

Time (mins)	Oxygen Absorption (mls/15 mins)	
	Experiment 1	Experiment 2
15	3.5	3.5
45	6.4	6.4
75	8.6	8.5
120	11.4	11.3

(iii) Modified Barcroft Apparatus.

This apparatus was used for the qualitative testing of the inhibitor or catalytic properties of added substances on the initial stage of the oxidation of tetralin at moderate temperatures. It was found especially useful when the reaction rate was low and oxygen absorption small (e.g. inhibited oxidations).

The apparatus is shown in Figure IV. It consisted of two 200 ml. side arm flasks fitted with an interconnecting tube equipped with a tap, and a butyl phthalate differential manometer. Inhibitor properties were studied by adding 10 mls. of tetralin to each flask, 0.3 ml. of the substance under investigation to the test flask, and then placing both flasks in a thermostat at 30°C. and fitting with efficient stoppers. The interconnecting tap was opened and after allowing fifteen minutes for attainment of steady conditions was then closed again. Thereafter, small differences in the rate of oxygen absorption in the two flasks were easily detected on the differential manometer.

Slightly smaller quantities of tetralin (5 mls.) were used for the investigation of the catalysis of oxygen uptake, and in those cases where it was found necessary to employ a solvent for the substance under investigation equal quantities of solvent were added to both the standard and test flasks to obviate errors of expansion.

III. EXPERIMENTAL RESULTS.

(a) General Characteristics of the Thermal Oxidation of Tetralin at 76°C.

The general characteristics of the oxidation were studied by the flow method. During the course of the oxidation at 76°C. the tetralin changed colour, becoming yellow, and then gradually darkened until after fifty hours it was reddish orange. Water was formed during the reaction, but no oxides of carbon could be detected in the off gases. The viscosity of the solution increased as the oxidation proceeded, and after eighty hours it had the consistency of a thick oil. The pH of the solution gradually decreased and samples from the later stages of the oxidation were strongly acidic. The peroxide content of the oxidising hydrocarbon was determined at frequent intervals, and results showing the variation of the peroxide concentration with the period of oxidation are shown in Table III and illustrated in Figure V.

Table III.

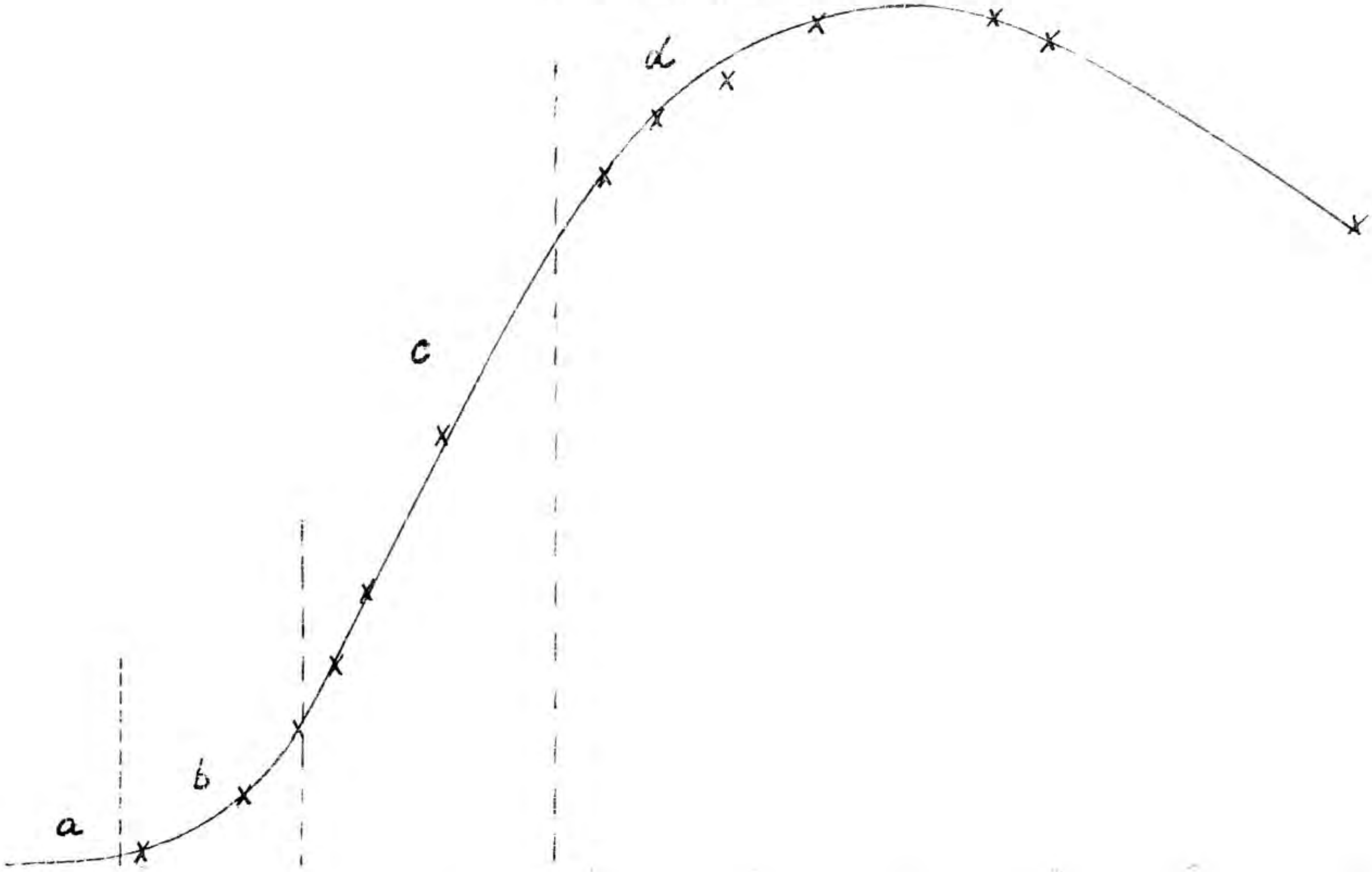
The Oxidation of Tetralin at 76°C.

Time (hrs)	0	9	16	19.5	22	24	29
Tetralin Hydroperoxide (gms/ml.)	0	.005	.028	.054	.081	.113	.177

Time (hrs)	40	43.5	48	54	66	69.5	90
Tetralin Hydroperoxide (gms/ml.)	.282	.306	.321	.345	.346	.337	.261

[illegible]

[illegible]


a
b
c
d

It appeared from Figure V that the oxidation took place in a number of successive stages and could be subdivided in the following manner:-

Stage (a)

The reaction was slow but was nevertheless definite. Peroxide formation could be detected from the very outset and its concentration gradually increased with time.

Stage (b)

The rate of peroxide formation gradually increased and the autocatalytic nature of the reaction became evident.

Stage (c)

The rate of peroxide formation reached a constant value and the reaction settled down to a steady state for a number of hours.

Stage (d)

The rate of peroxide formation gradually decreased, the product having darkened in colour and become both viscous and acidic.

Figure V(a)(b) is typical of an autocatalytic reaction and similar curves have been obtained for the oxidation of hydrocarbons of varying type. Larsen, Thorpe and Armfield(110), however, who investigated the liquid phase oxidation of tetralin, could find no evidence of autocatalysis. They suggested that tetralin exhibited auto-inhibition and Figure VI illustrates their results showing a gradual decrease in the rate of the reaction as indicated by oxygen uptake.

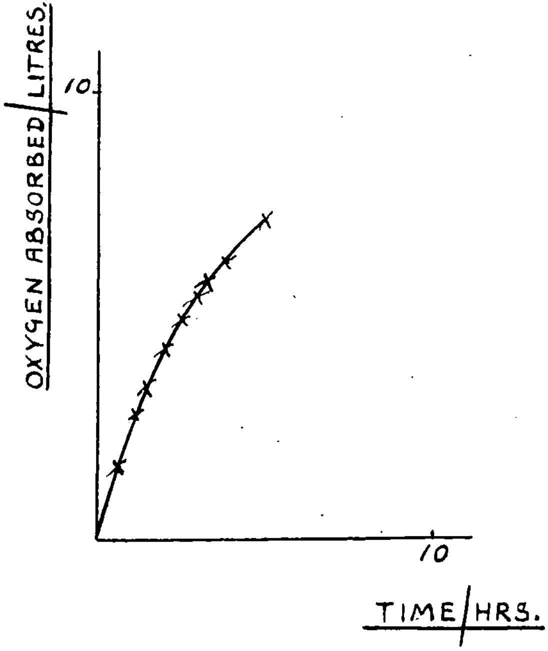


Figure VI.

/The Oxidation of Tetralin at 110°C.
(Larsen, Thorpe and Armfield)/

The temperature at which they carried out their investigation was 110°C. and both the induction period and the period of autocatalytic acceleration of a substance such as tetralin, which is so susceptible to oxidation, would, at this temperature, be greatly shortened and tend to pass unobserved. This is clearly demonstrated by Figure VII which shows the results obtained by Medvedev and Podyapolskaya(93) for the rate of oxygen uptake by tetralin at varying temperatures. The autocatalysis, although clearly evident up to 85°C., is hardly discernible at 95°C., and at 110°C. would undoubtedly tend to pass unobserved.

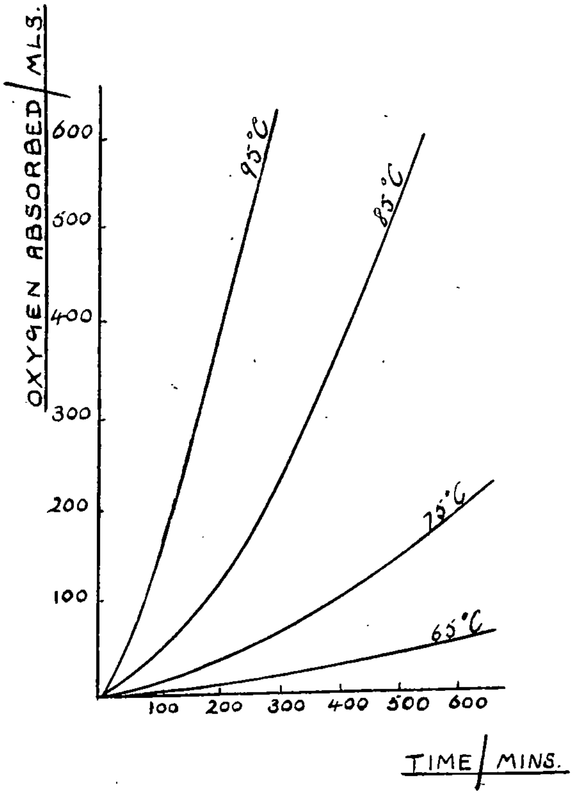


Figure VII.

[The Oxidation of Tetralin (Medvedev and Podyapolskaya)]

Figure VI thus represents the same sequence of the oxidation as Figure V(c) and (d) in which the reaction has already reached a steady state.

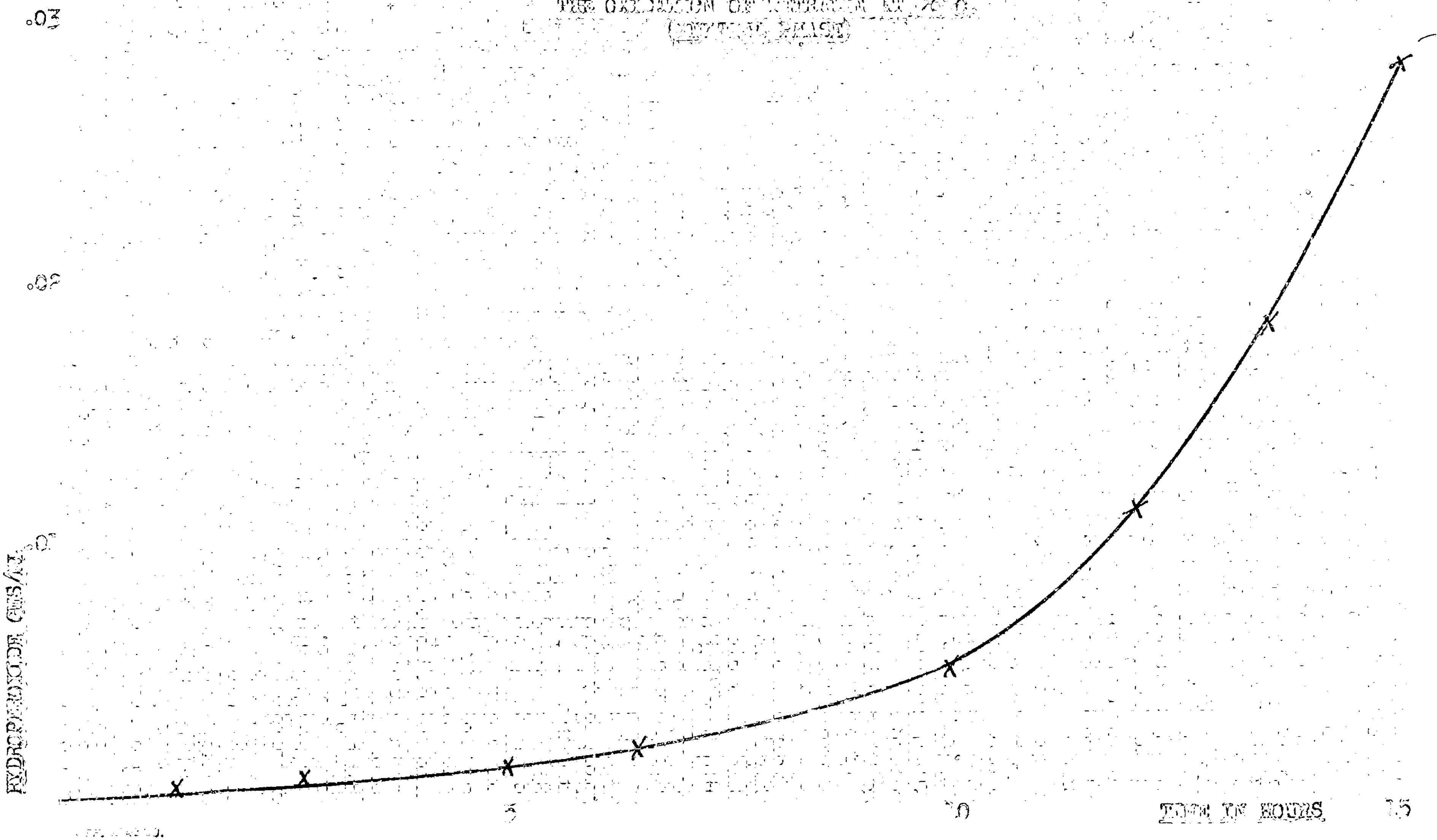
Such results emphasise the necessity for carrying out investigations at the lowest temperature concomitant with an accurate measurement of both peroxide formation and oxygen uptake, in order that the separate stages of the reaction can be clearly recognised and the effect of secondary products minimised. The observations of Medvedev and Podyapolskaya and Balsbaugh and Oncley(111) who investigated the oxidation of tetralin at lower temperatures (30-65°C.) and obtained a gradual acceleration in the rate of oxygen uptake and peroxide formation confirm the autocatalytic nature of the oxidation of tetralin.

(b) The Initial Phase of the Oxidation.

Stage (a) and part of stage (b) of Figure V are usually termed the induction period. The duration of stage (a) can be greatly influenced by temperature, the type of apparatus, and the addition of catalysts or the presence of impurities. Stephens(112) has suggested that induction periods are not related to a growth of the peroxide concentration in the system but are caused by the presence of impurities. Evidence to the contrary exists, however, and Stephens himself still observed induction periods with cyclohexene even after rigorous purification, and Wagner and Hyman(105) failed to eliminate the induction period from a purified sample of isopropyl benzene as did Henderson and Young(113) with oleic acid. It seems probable that many of the so-called induction periods that are observed are related to the presence of inhibitor impurities. Nevertheless, when this type of induction period has been eliminated by purification, most hydrocarbons undergoing low temperature oxidation still exhibit a period of a low rate of oxygen uptake prior to attaining a constant rate at a higher level. This latter type of induction period should be differentiated from the former, and some confusion exists because of the common terminology. The former type of induction period

Figure VIII.

THE OXIDATION OF TETRALIN AT 76° C.
(INITIAL PHASE)



caused by the presence of impurities is simply an example of an inhibited oxidation in which no reaction is apparent and which, once all the inhibitor has been destroyed, will be followed by the latter type of induction period which cannot be rigidly separated from the period of autocatalytic acceleration. It may be regarded as a period of comparatively slow but nevertheless definite reaction which proceeds with a gradually increasing rate and during which there is an accumulation of peroxide (if this is sufficiently stable) in the system. Table IV shows the results of peroxide determinations in the early stages of the oxidation and demonstrates the formation of peroxide at the very outset of the reaction. These results are illustrated in Figure VIII in which the autocatalytic acceleration can be clearly seen.

Table IV.

The Oxidation of Tetralin at 76°C

Time (hrs)	0	1.3	2.75	5	6.5	10	12	13.5	15
Tetralin Hydroperoxide (gms/ml.)	0	.0004	.0009	.0013	.002	.005	.011	.018	.028

The fact that hydroperoxide formation could be detected in even the earliest stages of the oxidation suggested the high probability that tetralin hydroperoxide was a primary product of the reaction. The relationship between the amounts of oxygen absorbed and tetralin hydroperoxide formed was therefore investigated. A series of experiments were carried out in the static apparatus and the hydroperoxide concentration and oxygen uptake measured during stages (a) and (b) and part of stage (c) of Figure V. At various stages samples were taken for peroxide analysis and thus the total peroxide content was computed. After a measured volume of oxygen had been absorbed the peroxide analysis was repeated and the increase in the total peroxide content calculated. Results are shown in Table V and illustrated in Figure IX.

Table V.

(1)	Weight of Tetralin	29.920 gms
	" " Hydroperoxide in 1.017 gms sample after O_2 absorption	0.0119 "
	∴ Total weight of Hydroperoxide formed during O_2 absorption	0.350 "
	Volume of Oxygen absorbed (N.T.P.)	48.6 mls
	∴ Oxygen accounted for as Hydroperoxide	98%
(2)	Weight of Tetralin	28.203 gms
	" " Hydroperoxide in 1.017 gms sample	0.0119 "
	Total initial weight of Hydroperoxide	0.330 "
	Weight of Hydroperoxide in 1.195 gms sample after O_2 absorption	0.030 "
	Total weight of Hydroperoxide after O_2 absorption	0.708 "
	∴ Increase in weight of Hydroperoxide present	0.378 "
	Volume of Oxygen absorbed (N.T.P.)	51.6 mls
	∴ Oxygen accounted for as Hydroperoxide	98.2%

(Cont'd)

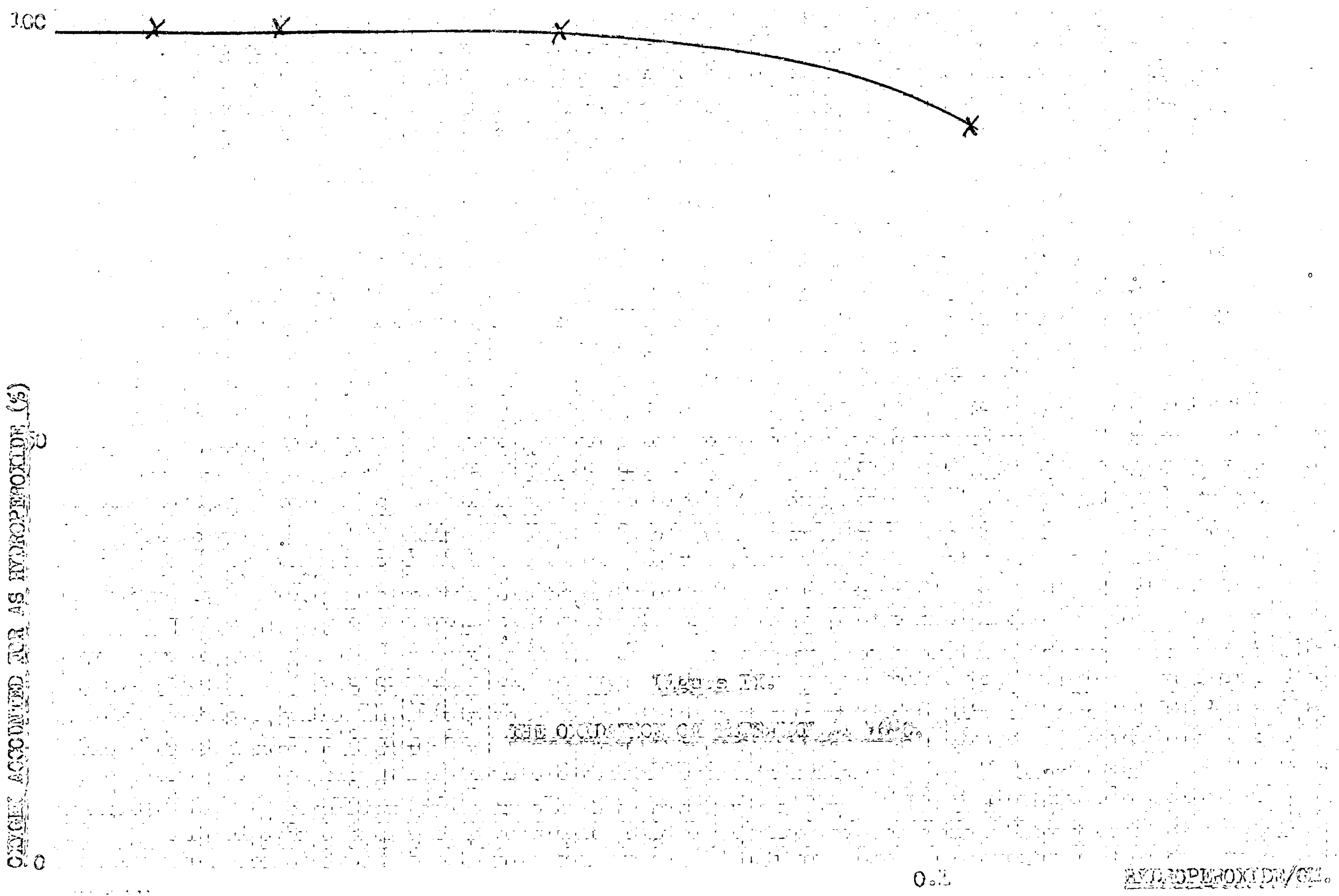


Figure IX.

THE OXIDATION OF [illegible] AT 70°C.

Table V. (Cont'd)

(3)	Weight of Tetralin	29.280 gms
	" " Hydroperoxide in 0.9267 gm. sample	0.0312 "
	Total initial weight of Hydroperoxide	0.988 "
	Weight of Hydroperoxide in 2.6145 gms sample after O_2 absorption	0.152 "
	Total weight of Hydroperoxide after O_2 absorption	1.705 "
	.˙. Increase in weight of Hydroperoxide present	0.717 "
	Volume of Oxygen absorbed (N.T.P.)	100 mls
	.˙. Oxygen accounted for as Hydroperoxide	98%
(4)	Weight of Tetralin	27.322 gms
	" " Hydroperoxide in 0.946 gm. sample	0.075 "
	Total initial weight of Hydroperoxide	2.166 "
	Weight of Hydroperoxide in 0.931 gm. sample after O_2 absorption	0.0978 "
	Total weight of Hydroperoxide after O_2 absorption	2.870 "
	.˙. Increase in weight of Hydroperoxide present	0.704 "
	Volume of Oxygen absorbed (N.T.P.)	111 mls
	.˙. Oxygen accounted for as Hydroperoxide	86.4%
(5)	Weight of Tetralin	26.380 gms
	Weight of Hydroperoxide in 0.9566 gm. sample	0.196 "
	Total initial weight of Hydroperoxide	5.402 "
	Weight of Hydroperoxide in 0.9164 gm. sample after O_2 absorption	0.206 "
	Total weight of Hydroperoxide after O_2 absorption	5.926 "
	.˙. Increase in weight of Hydroperoxide present	0.524 "
	Volume of Oxygen absorbed (N.T.P.)	83.2 mls
	.˙. Oxygen accounted for as Hydroperoxide	86.1%

It can be seen from Figure IX that all the oxygen absorbed in the initial phase of the reaction could be accounted for by the formation of the hydroperoxide. In later stages of the oxidation when secondary reactions became more marked, the percentage of oxygen absorbed which could be thus accounted for decreased.

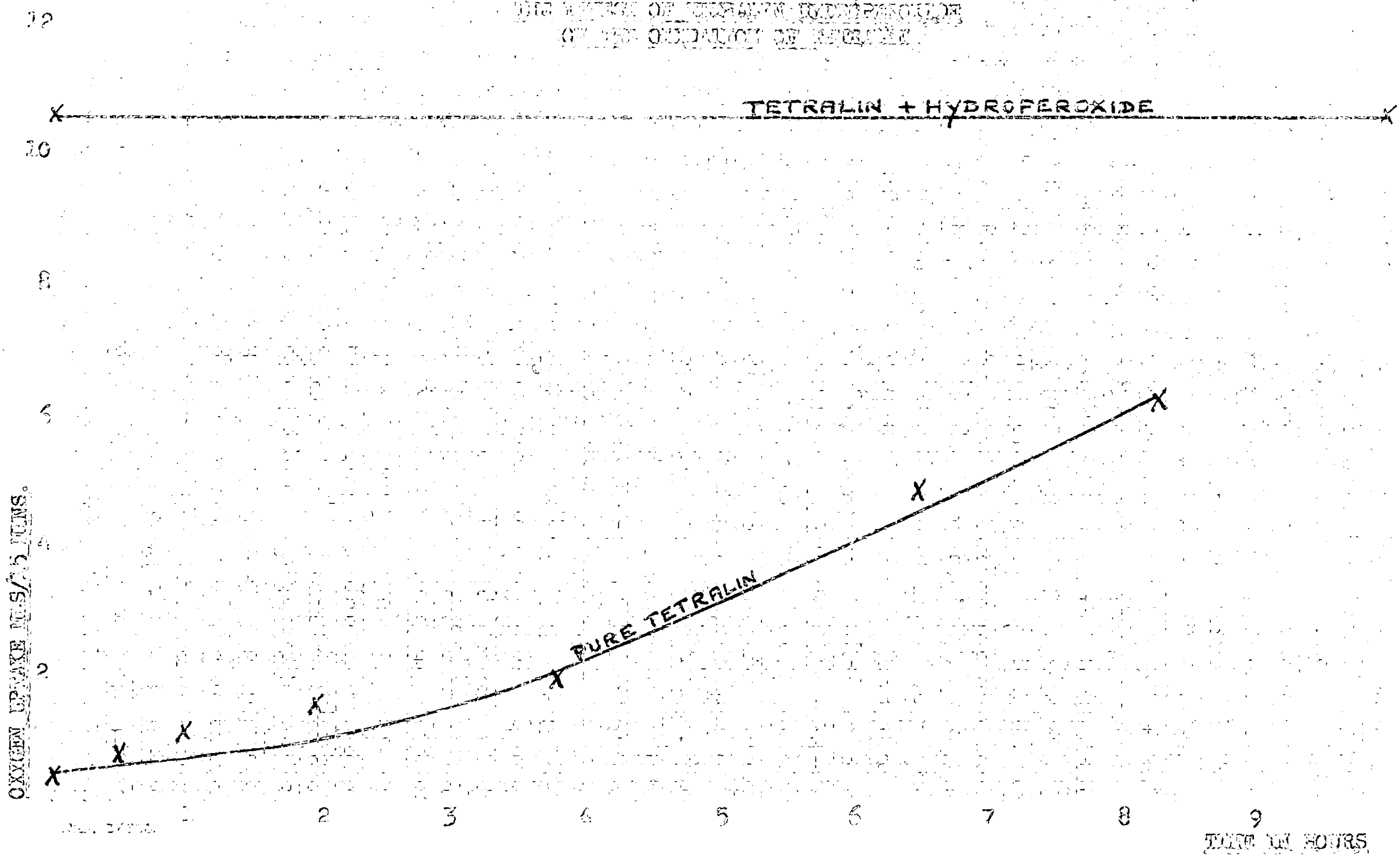
Similar stoichiometric relationships between oxygen absorption and peroxide formation in the first phase of autoxidation have been observed with both aldehydic and unsaturated substances. Farmer and Sutton(29) investigated the autoxidation of polyisoprenes and showed that in the case of dihydrofarnesene all the absorbed oxygen up to an intake of 6% was found to be peroxidic. Henderson and Young(113) and Almquist and Branch(114) obtained similar results with oleic acid and benzaldehyde, and Bolland(115) showed that in the oxidation of ethyl linoleate all the oxygen absorbed up to 0.4 gm. mol./gm. mol. was used in the formation of hydroperoxide groups. It is evident that a strong similarity exists between the autoxidation of the CH_2 group in tetralin and the autoxidation of α methylenic groups in olefinic substances and the CHO group of benzaldehyde.

(c) The Role of Tetralin Hydroperoxide.

Medvedev and Podyapolskaya related the autocatalytic nature of the oxidation of tetralin to the accumulation of the hydroperoxide in the system and suggested that chain initiators were formed when the hydroperoxide decomposed. If tetralin hydroperoxide was capable of producing chain initiators then it should function as a catalyst for the oxidation of tetralin, and this was investigated by measuring the rate of oxygen uptake of a sample of tetralin to which pure tetralin hydroperoxide had been added in the static

Figure X.

THE EFFECT OF TETRALIN HYDROPEROXIDE
ON THE OXIDATION OF TETRALIN.



apparatus at 76°C. Results are shown in Table VI below:-

Table VI.

The Effect of Tetralin Hydroperoxide on the Oxidation of Tetralin.

Time (hrs)	Oxygen Uptake mls/15 mins.	
	Hydrocarbon	Hydrocarbon + 1 gm. Hydroperoxide
0	0.3	10.5
0.5	0.7	"
1.0	1.1	"
2.0	1.4	"
3.75	1.8	"
6.5	4.8	"
8.3	6.1	"
20.0	10.5	-

Figure X, which illustrates the variation of oxygen uptake with time for both the pure hydrocarbon and a sample to which the hydroperoxide had been added, shows that the induction period was entirely eliminated and that if sufficient hydroperoxide was added it was possible to pass immediately to stage (c) (Figure V) of the oxidation - the period of steady reaction.

This confirmation of Medvedev and Podyapolskaya's observation that tetralin hydroperoxide was a catalyst for the oxidation of tetralin, which was contrary to the findings of George and Robertson(95), demands a re-examination of the experimental data supplied by these latter. George and Robertson investigated the effect of the addition of the hydroperoxide at 65°C. and 108°C.

At 108°C. they stated that the addition of up to 0.7% of the hydroperoxide had an extremely small effect on the initial rate of oxidation. The criticisms previously made of the investigation of the oxidation by Larsen, Thorpe and Armfield(110) at 110°C. are equally applicable to the work of George and Robertson at 108°C. Induction periods are not detectable at this temperature and autocatalytic effects are hardly discernible. It is therefore not surprising that changes in the duration of the induction and autocatalytic periods which are appreciable at lower temperatures should almost pass unobserved at 108°C. Nevertheless, an examination of George and Robertson's results (illustrated in Figure XI) reproduced from the Proceedings of the Royal Society, 1946, 185, p.312, shows that the effect of added hydroperoxide is far from negligible even at this temperature. It can be seen that the addition of 0.7% of tetralin hydroperoxide produced an increase in the initial rate of oxidation which was 30% higher than that obtained with the pure hydrocarbon.

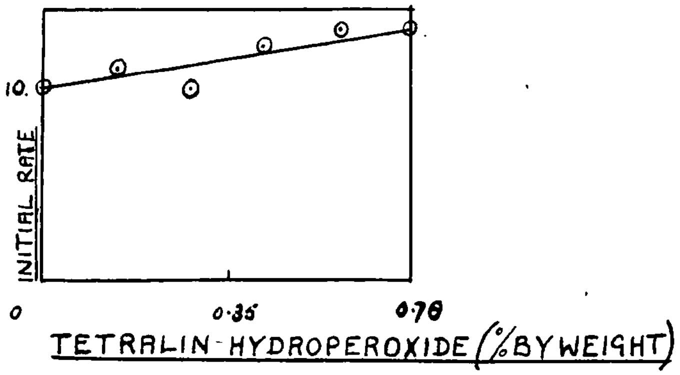


Figure XI.

The Effect of Tetralin Hydroperoxide on the Oxidation of Tetralin at 108°C. (George and Robertson)

Figure XII. shows the results obtained by the same workers when the hydroperoxide was added to tetralin at 65°C. They concluded that there was a small increase in rate up to a maximum value as the initial hydroperoxide concentration was increased.

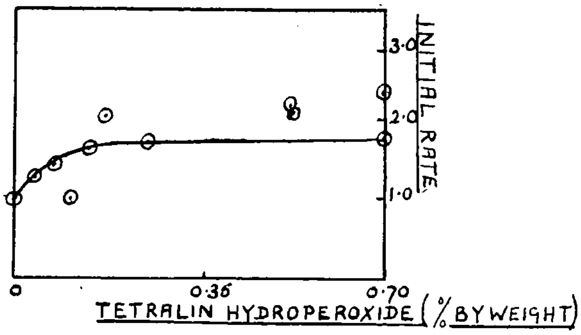


Figure XII.

The Effect of Tetralin Hydroperoxide on the Oxidation of Tetralin at 65°C. (George and Robertson)

George and Robertson pointed out that the results they obtained at 65°C. were somewhat irreproducible. This is not surprising since, because of the extremely small volume of hydrocarbon employed (1 ml.), only 0.6 ml. of oxygen needed to be absorbed to produce a hydroperoxide concentration of 0.35%. In view of the tendency towards inaccuracy of the experiments involving the very small hydroperoxide additions and the favourable scatter of points for the larger hydroperoxide additions, the variation of the initial oxidation rate with hydroperoxide concentration would be better represented by Figure XIII.

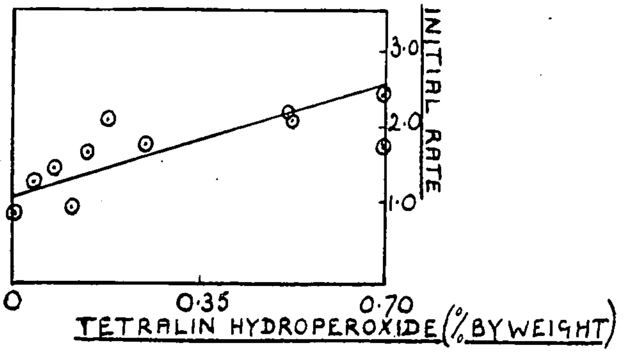


Figure XIII.

The Effect of Tetralin Hydroperoxide on the Oxidation of Tetralin at 65°C.

It can be seen from Figure XIII that as the concentration of added hydroperoxide is increased the initial rate shows a corresponding increase until at a concentration of 0.7% the initial rate of oxidation is 150% higher than that obtained with the pure hydrocarbon. The use of oxidised solutions of tetralin as a source of the hydroperoxide instead of the pure crystalline hydroperoxide is another possible cause of error in the work of George and Robertson. Such solutions probably contain secondary oxidation products which can adversely influence the reaction, and Ivanov and co-workers(85) have attributed the anomalous results obtained by Yamada(116), when investigating the kinetics of the decomposition of tetralin hydroperoxide, to this cause.

It has been shown that the autocatalytic nature of the oxidation of tetralin is intimately connected with the increase in the concentration of the primary intermediate product, tetralin hydroperoxide, and it is of interest to compare such experimental evidence with Semenoff's(117) theoretical treatment of hydrocarbon oxidation. Semenoff(117a) divided hydrocarbons and aldehydes into two groups according to their kinetic behaviour. The oxidation of the first group he characterised by (a) an exponential growth of the reaction rate 'W' with time during the first stages of the reaction according to the expression $W = Ce^{\phi t}$ where C and ϕ are constants and (b) the existence of a maximum velocity at the moment of half change after which the reaction slows down. The oxidation of the second group of hydrocarbons after a short induction period attains a constant rate of reaction. Differentiation between ordinary chain reactions and the above types which Semenoff terms chains with degenerate branching is possible only by an examination of the reaction velocity-time curve. If the curve is concave and corresponds to the law $W = Ce^{\phi t}$, then the reaction is probably of the degenerate chain type. Semenoff's(117b) theory of chains with degenerate branching involved the rapid development of a primary chain which resulted in the formation of a relatively stable intermediate product. This intermediate product could then react independently to give the final product, and in the process of this decomposition Semenoff suggested that initiators could be formed which could restart the primary chain.

The shape of the rate/time graph for tetralin is concave and it follows that the oxidation must involve a chain reaction of the degenerate branching type. George and Robertson applied the Semenov formula rate = $Ce^{\phi t}$ to their results and found that tetralin obeyed this relationship for the first 10% of the reaction at 120°C. The higher degree of degenerate chain branching observed by Semenov(117c) for the gas phase oxidation of paraffins (the equation $W = Ce^{\phi t}$ was obeyed over 40% of the reaction) can be explained by the lack of stability of intermediate peroxides which are formed in comparison with the relatively high thermal stability of tetralin hydroperoxide. George and Robertson suggested that degenerate chain branching in the liquid phase oxidation of tetralin was more marked the lower the temperature. If degenerate chain branching occurs as the result of the decomposition of the intermediate product produced by the primary chain, it follows that an increase in chain branching as the temperature is decreased implies that the rate of decomposition of the intermediate product undergoes a corresponding increase, but this is not in agreement with observed experimental facts. An alternative solution is that chain initiators can, at higher temperatures, undergo rapid reaction before they are able to function as such, and this suggestion will be considered in further detail in Section V. It is possible, however, that degenerate chain branching appears to decrease with an increased temperature of oxidation because of a greater tendency for fission to occur in the naphthenic ring as a result of hydroperoxide decomposition, with the consequent production of phenolic compounds which could then exert a considerable inhibitor effect (see Section VI). Rapid production of α tetralone at higher temperatures would increase this effect for Medvedev and Podyapolskaya have shown that it can also function as an inhibitor of the oxidation.

(d) The Steady State Reaction.

It has been shown in Figure V(c) that after an initial autocatalytic acceleration the oxidation of tetralin settled down to a steady state in which the rate of peroxide formation became constant. The significance of the attainment of this steady state is that chain initiators produced by the chain branching reaction of decomposing tetralin hydroperoxide are just sufficient to balance the loss of initiators by normal chain breaking processes. In later stages of the reaction, Figure V(d), the rate of decomposition of the hydroperoxide becomes greater than its rate of formation and the hydroperoxide content of the system declines. The decrease in the rate of formation of the hydroperoxide in stage (d) of the reaction is related to the accumulation in the system of products which exert inhibitory action (see Section VI). This decrease in the reaction rate is further accentuated as the oxidation proceeds by the diminution in hydrocarbon

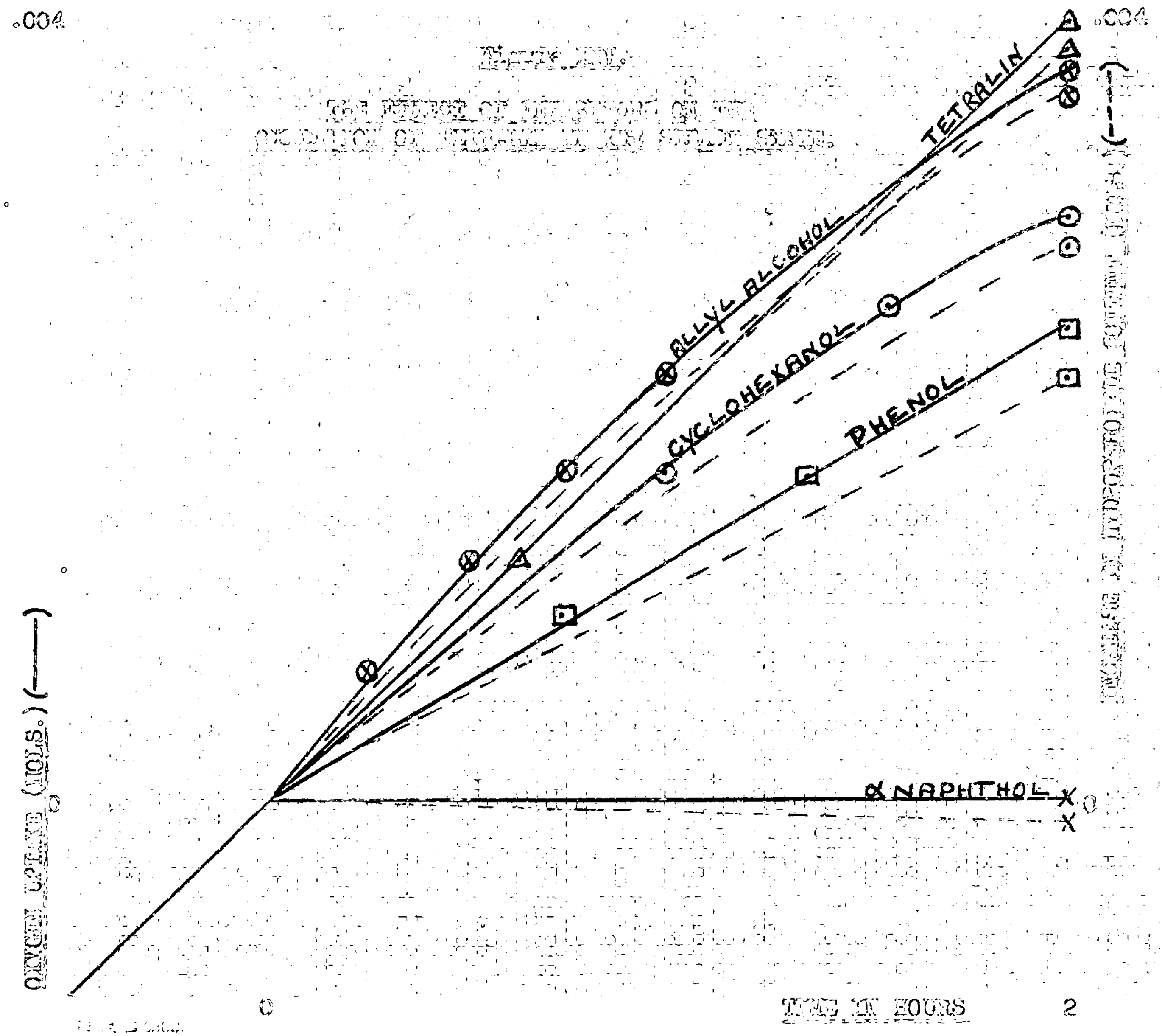


Figure [illegible].

THE EFFECT OF [illegible] ON THE

OXIDATION OF [illegible]

concentration for George and Robertson have shown that the reaction rate is proportional to the square of the hydrocarbon concentration.

The investigation of the steady state reaction was facilitated by the observation that the conditions of the steady state could be reproduced without awaiting a long preliminary oxidation period by the addition of a sufficient quantity of tetralin hydroperoxide. The effect of the addition of a number of alcohols, phenols, and hydrocarbons on the steady state reaction was investigated in the static apparatus. The conditions of the steady state were reproduced by the addition of 1 gm. of tetralin hydroperoxide to 30 mls. of tetralin. The oxygen uptake rate was then checked and 1 ml. or 1 gm. samples of the substance under investigation added by manipulation of the ball valve. The effect of the addition of the same substances on the initial stages of the reaction was investigated in the Barcroft's apparatus. The results of the addition of a number of alcohols, phenols, and hydrocarbons in the steady state are shown in Table VII, and Figure XIV illustrates typical examples. Many workers have reported that alcohols can exert a considerable inhibitor effect on the initial stages of autoxidation reactions, and this is confirmed by the results shown in Table VII. The anomalous results obtained with ethylene glycol and tertiary butyl alcohol most probably arose from very small traces of water which would seriously interfere with the accuracy of this method. As can be observed from Table VII, the effect of alcohol addition in the steady state was not marked and led to only a slight decrease in the rate of oxygen uptake. In nearly all cases a high percentage of the oxygen absorbed was still utilised in the formation of peroxide. The lower value obtained with ethylene glycol may have been due to the extreme difficulty of obtaining a uniform sample for analysis because of the imiscibility in tetralin. It is also feasible, however, that the lower value may have been related to the possible incidence of glycol splitting by intermediate free radicals (see Section V). The high percentage of oxygen which can be accounted for as hydroperoxide and the apparent lack of attack on the carbinol group confirms the view that the oxygen absorbed is almost entirely utilised in hydroperoxide formation and not in further oxidation processes of the type:-

$$>CH_2 \longrightarrow >CH(OH) \longrightarrow >C=O$$

Evidence of attack on alcohols by free radicals with consequent ketone formation has been observed, however, (see Section V).

Phenol which has been reported as an efficient inhibitor of autoxidations had surprisingly little effect when added in the steady state. α Naphthol, however, brought about a complete cessation of oxygen absorption. Cyclohexene, which is itself capable of undergoing autoxidation, had little effect on the steady state reaction, but both anthracene and

Table VII.

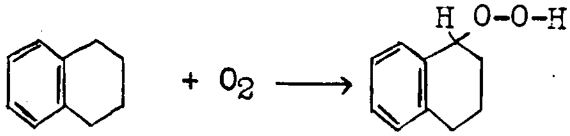
Effect of Alcohols, Phenols and Hydrocarbons on the Autoxidation of Tetralin.

Substance Added	Initial Reactivity	Effect on Steady State Oxygen Uptake mls/15 mins		Effect on Oxygen Uptake expressed as a percentage	Percentage of Oxygen absorbed accounted for as Hydroperoxide
		Before Addition	2 hrs after Addition		
Ethylene Glycol	Increased	10.5	9.0	14 decrease	70
αTetralol	Inhibited	"	8.6	23 "	89
Benzyl Alcohol	"	"	9.6	9 "	90
n-Butanol	"	"	10.3	No effect	95
iso-Propanol	No effect	"	7.4	30 decrease	92
tert-Butanol	Increased	"	8.8	13 "	87
cyclo-Hexanol	Inhibited	"	9.8	7 "	97
Allyl Alcohol	"	"	8.0	23 " (Rate initially increased then declined)	97
Phenol (1%)	"	"	7.5	30 decrease	95
αNaphthol (1.3%)	"	"	-	Complete Inhibition	-
Cyclohexene	Increased	"	11.4	9 increase	97
Anthracene	Inhibited	"	6.8	35 decrease	93
Phenanthrene	"	"	8.0	23 "	93
Fluorene	No effect	"	9.0	14 "	98

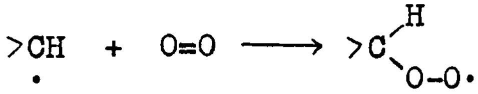
phenanthrene brought about a gradual reduction in the rate of oxygen absorption. This decrease in oxygen absorption was probably caused by the inhibitor action of anthraquinone and phenanthraquinone which Milas(118) has shown are produced by induced oxidation when anthracene and phenanthrene are used as inhibitors. French, Olcott and Mattill(119) also observed that the efficiency of inhibitors of the autoxidation of fats gradually decreased as the amount of peroxide in the system prior to inhibitor addition was increased, and they suggested that this was due to a mutual destruction of peroxide and inhibitor. Wagner and Brier(120) studied the effect of hydroquinone on the rate of oxidation of linseed oil and found that it prolonged the induction period in proportion to the amount added; once the induction period was over, however, further additions of hydroquinone were without effect. Theories have been advanced suggesting that inhibitors function by bringing about the decomposition of intermediate peroxides, but this is not the case with tetralin because, although the addition of α naphthol completely inhibited the oxidation, no large decrease in the peroxide content of the system could be detected. It is much more probable that in the initial stages of the oxidation when the peroxide concentration is low inhibitors can seriously affect chain starting and termination processes. When the peroxide concentration increases, however, and a constant supply of chain initiators is obtained by a steady peroxide decomposition, inhibitors are less effective. The mechanism and kinetic implications of this aspect of inhibition are discussed in Section VII).

IV. INVESTIGATION OF THE MECHANISM OF THE INITIAL PHASE OF THE AUTOXIDATION.

It was shown in Section III(b) that tetralin hydroperoxide was the primary isolable product of the autoxidation of tetralin. The initial phase of the reaction may, therefore, be regarded as:-

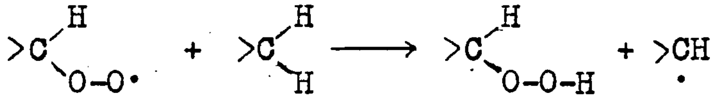


The oxidation exhibited the kinetic characteristics of a typical autocatalytic reaction and was catalysed by the addition of tetralin hydroperoxide. The susceptibility of the autoxidation to catalysis and inhibition suggested that it possessed a chain mechanism, and catalysis by the hydroperoxide indicated that the chain carriers were possibly free radicals. The following chain process has been postulated for the main chain sequence of the oxidation of hydrocarbons by a number of workers(55, 56, 57).



$$>\underset{\bullet}{\mathrm{CH}} + \mathrm{O{=}O} \longrightarrow >\mathrm{C}\begin{matrix}\mathrm{H}\\ \mathrm{O{-}O\cdot}\end{matrix} \qquad (1)$$

Radical R_1 Radical R_2



$$>\mathrm{C}\begin{matrix}\mathrm{H}\\ \mathrm{O{-}O\cdot}\end{matrix} + >\mathrm{C}\begin{matrix}\mathrm{H}\\ \mathrm{H}\end{matrix} \longrightarrow >\mathrm{C}\begin{matrix}\mathrm{H}\\ \mathrm{O{-}O{-}H}\end{matrix} + >\underset{\bullet}{\mathrm{CH}} \qquad (2)$$

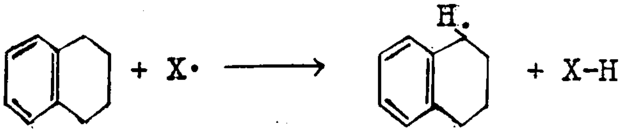
Radical R_2 Hydrocarbon Hydroperoxide Radical R_1

The chain starting reaction for such a process must account for the formation of the hydrocarbon radical R_1 and may be generally represented by a reaction of the type:-

$$\underset{\text{(Catalyst)}}{X\cdot} \; + \; >CH_2 \longrightarrow X\text{-}H \; + \; \underset{R_1}{\underset{\bullet}{>CH}} \qquad (3)$$

The hydrocarbon radical R_1 thus produced can react with oxygen to form the hydroperoxide radical R_2: this latter then reacts with a molecule of the hydrocarbon to produce a hydroperoxide molecule and regenerate the radical R_1 to restart the oxidation cycle.

If such a chain process is applicable to the oxidation of tetralin, then all substances which are capable of abstracting atomic hydrogen (H·) from the tetralin molecule to produce the tetralyl radical:-



should, if not influenced by external factors (e.g. inhibition by reaction products), be capable of promoting an accelerated rate of reaction marked by an increase in the rate of oxygen absorption.

The strongly electrophillic nature of free aryl radicals suggests their use as such dehydrogenators. The observation by George$^{(121)}$ that dibenzoyl peroxide can catalyse the oxidation of tetralin gives support for the reaction scheme involving equations (1), (2) and (3), because Hey and Waters$^{(122)}$ have shown that there is strong evidence that dibenzoyl peroxide can, under suitable conditions, undergo decomposition with the production of free radicals. They suggested that the initial stage of the reaction could be represented by the equation:-

$$(C_6H_5CO)_2O_2 \longrightarrow C_6H_5\cdot + C_6H_5COO\cdot + CO_2$$

Reynhart(123) maintained that it was unnecessary to postulate the presence of free radicals to explain the decomposition of the peroxide, but strong experimental evidence for the participation of free radicals in the reaction has been obtained by Cuthbertson et al(124), and the widespread use of dibenzoyl peroxide as a catalyst for polymerisation processes offers further strong support for this viewpoint. Assuming the Hey and Waters' theory to be correct, free phenyl radicals formed by the decomposition of the peroxide could act as the catalyst X· in equation (3) and produce the tetralyl radical which could then take part in the main chain cycle (equations (1) and (2)), thus accounting for the catalysis observed by George. Further evidence supporting this chain sequence was obtained by investigating the effect of a series of selected compounds on the initial rate of oxygen uptake. Compounds were selected either because they were oxidising or dehydrogenating agents or could, under suitable conditions, undergo decomposition with the production of free radicals.

Catalysis by Free Radicals.

Benzene Diazoacetate.

Benzene iso(anti)-diazoacetate has been shown by Grieve and Hey(125) to be tautomeric with N.nitroso acetanilide:-

$$Ph\cdot N(NO)\cdot CO\cdot CH_3 \rightleftharpoons Ph\cdot N{:}N\cdot O\cdot CO\cdot CH_3$$

and it was prepared as the labile tautomer using a method described by the same workers. Nitrous fumes were passed into a 20% solution of acetanilide in glacial acetic acid until a dark green colour developed. The solution was poured into water and the resultant yellow solid was filtered off and dried, first by suction and then on a porous tile. According to Grieve and Hey(125) and Waters(126) benzene diazoacetate can, in suitable solvents, undergo spontaneous decomposition with the production of free phenyl radicals:-

$$Ph\cdot N{:}N\cdot O\cdot CO\cdot CH_3 \longrightarrow Ph\cdot + N_2 + \cdot O\cdot CO\cdot CH_3$$

Free phenyl radicals thus formed should be capable of producing tetralyl radicals by reaction (3) which could then initiate the main cycle reactions (1) and (2).

0.9 gm. of benzene diazoacetate were, therefore, added to 80 mls of tetralin at room temperature and the oxygen absorption measured in the static apparatus. Oxygen uptake was immediately observed despite the fact that nitrogen evolved during the decomposition of the benzene diazoacetate tended to mask any decrease in volume. This catalysis of oxygen uptake continued only during the period that the benzene diazoacetate was decomposing and generating free phenyl radicals as chain initiators. As soon as the decomposition of the benzene diazoacetate ceased, the rate of oxygen uptake dropped to a very low level again. The level to which the oxygen uptake rate decreased when the supply of phenyl radicals ceased was dependent upon the quantity of tetralin hydroperoxide formed during the interim period since, as was shown in Section III(c), the hydroperoxide itself can function as a catalyst of the oxidation.

Lead Tetra-acetate.

Solutions of lead tetra-acetate in glacial acetic acid decompose with the production of free acetate and possibly free methyl radicals(127):-

$$Pb(O{\cdot}CO{\cdot}CH_3)_4 \longrightarrow Pb(O{\cdot}CO{\cdot}CH_3)_2 + 2\ {\cdot}O{\cdot}CO{\cdot}CH_3$$

$${\cdot}O{\cdot}CO{\cdot}CH_3 \longrightarrow CO_2 + {\cdot}CH_3$$

and should, therefore, be capable of producing tetralyl radicals by reaction (3) and thus catalyse the oxidation of tetralin.

One gm. of lead tetra-acetate was dissolved in 10 mls glacial acetic acid and added to 30 mls of tetralin at 76°C. A sodium hydroxide trap was incorporated in the static apparatus to absorb any carbon dioxide produced during the decomposition. Results shown in Table VIII show that appreciable catalysis of the oxidation took place during the period of decomposition of the lead tetra-acetate. A blank run checking the effect of the addition of glacial acetic acid showed that this reagent had a negligible effect on the reaction rate.

Triphenyl Methyl.

Ziegler et al(41, 42) have shown that the free radical triphenyl methyl can initiate the autoxidation of aldehydes and olefinic substances, and a sample was prepared for investigation by treating a solution of triphenyl methyl chloride in benzene with silver powder in an atmosphere of carbon dioxide. Solids were removed by filtration in the same inert gas, and premature oxidation during sampling prevented by the use of a hypodermic syringe, the needle of which was pierced through the stopper of the container, and the transfer thus effected without exposure to the atmosphere. A quantity of the benzene solution equivalent to 0.2 gm. of triphenyl methyl was added to 30 mls of tetralin at room temperature in the static apparatus. Triphenyl methyl did not prove to be a catalyst for the oxidation at this temperature (Table VIII), and oxygen was only absorbed during the period of formation of triphenyl methyl peroxide. The temperature was then increased to 76°C. and a rapid absorption of oxygen which occurred was attributed to the catalytic effect of the triphenyl methyl peroxide then present in the system. It was, therefore, decided to prepare a pure sample of triphenyl methyl peroxide and test its properties as a catalyst for the oxidation.

Triphenyl Methyl Peroxide.

The triphenyl methyl peroxide was prepared by the aeration of a benzene solution of triphenyl methyl. After filtration and ether washing, 0.2 gm. of the peroxide was added to 30 mls of tetralin at 76°C. Oxygen absorption was instantaneous and continued during the period of decomposition of the peroxide. The rate of oxygen absorption gradually decreased as the oxidation proceeded and smaller quantities of triphenyl methyl peroxide were available to supply chain initiators (Table VIII).

Triphenyl methyl normally acts as a chain initiator via the peroxide radical:-

$$Ph_3C\cdot + O_2 \longrightarrow Ph_3C{-}O{-}O\cdot$$

and the failure of triphenyl methyl to catalyse the oxidation of tetralin is probably due to the great ease of oxidation of hexaphenyl ethane relative to tetralin, so that the peroxide radical $Ph_3C{-}O{-}O\cdot$ never attains a sufficiently high concentration to act as a chain initiator in reaction (3). On the other hand, triphenyl methyl peroxide, which at 76°C. slowly decomposes to $Ph_3C{-}O\cdot$ radicals:-

$$Ph_3C{-}O{-}O{-}CPh_3 \longrightarrow 2\ Ph_3C{-}O\cdot\ ,$$

can fulfil the role of a chain initiator with high efficiency.

Zinc Chloride Benzene Diazonium Chloride Double Salt.

Waters(128) has shown that reactions of neutral acetone suspensions of diazonium chlorides with certain elements (such as mercury, antimony, and tellurium) indicate that the mechanism of the decomposition of diazonium chlorides under suitable conditions is non-ionic and involves isomerisation of the diazonium salt to the covalent diazo-chloride, homolytic decomposition of the latter then taking place:-

$$(PhN_2)^+ Cl^- \longrightarrow Ph{\cdot}N{:}NCl$$

$$Ph{\cdot}N{:}NCl \longrightarrow Ph{\cdot} + N_2 + Cl{\cdot}$$

Phenyl radicals produced by such a decomposition should be capable of initiating reaction (3) in the oxidation sequence. The simplest and smoothest way of generating phenyl radicals by this type of decomposition is achieved by employing metallic chloride double salts of the diazonium chloride. The zinc double salt of benzene diazonium chloride is suitable for this purpose and was prepared by the method of Makin and Waters(129). Five gms of aniline were diazotised in aqueous solution and after filtration were added to a solution of 6 gms of zinc chloride in concentrated hydrochloric acid. The crystalline double zinc diazonium chloride was filtered, lightly washed with acetone and dried.

The product was insoluble in tetralin and the addition of 1 gm. to 30 mls of tetralin had no catalytic effect on the oxidation at room temperature. A repetition of the experiment using acetone as solvent also gave negative results. Attempts to promote a slow decomposition of the double salt by gently increasing the temperature of the oxidation did not prove feasible because of the violent nature of the reaction, and a rapid gas evolution prevented any observation of oxygen uptake.

Phenyl Magnesium Bromide.

Evidence has been obtained by Kharasch and co-workers(130) that Grignard reagents can dissociate to free alkyl or aryl radicals, and it was decided to investigate the catalytic properties of phenyl magnesium bromide as a chain initiator. Phenyl magnesium bromide was prepared in an atmosphere of nitrogen by the reaction of 1.6 gms of magnesium in a mixture of 10 gms of bromobenzene and 50 ccs. of ether. Fifty mls of benzene (Analar) were then added and the ether removed in a stream of nitrogen. Five mls of the solution of phenyl magnesium bromide in benzene were added to 30 mls of tetralin at 76°C. There was a rapid absorption of approximately 15 mls of oxygen and the reaction then ceased. Gilman and Wood(131) have reported that Grignard reagents react readily with molecular oxygen with the formation of compounds of the type R·O·MgX. Such a reaction would undoubtedly be favoured under the experimental conditions described and would prevent the generation of free radicals.

Table VIII.

The Effect of Free Radicals on the Autoxidation of Tetralin.

Substance Added	Temp. °C.	Oxygen Uptake mls/15 mins					Effect
		Time after addition					
		15 mins	30 mins	45 mins	90 mins	120 mins	
Tetralin (Blank)	76	0.5	0.7	0.9	1.2	1.4	-
Benzene diazoacetate	17	9.5	9.5	9.0	5.0	-	Catalysis
Lead tetra-acetate	76	10.0		11.0	11.0	6.0	Catalysis
Triphenyl methyl	17	16.0	-				-
Triphenyl methyl peroxide	76	22.0		24.0		13.0	Catalysis
Zinc chloride benzene diazonium chloride	30	Gas Evolution					-
Phenyl magnesium bromide	76	16.0	-				-
Glacial Acetic Acid (Solvent)	76	0.5				0.9	-

Positive Halogen Compounds.

Positive halogen compounds which are characterised experimentally by their ability to liberate iodine from hydriodic acid are so called because they may be represented as acting by heterolytic bond fission to give halogen cations rather than anions.

Thus: $Cl\text{-}CH_2\text{-}CO\text{-}R \longrightarrow \overset{-}{C}H_2\text{-}CO\text{-}R + \overset{+}{Cl}$

$$Cl^+ + 2I^- \longrightarrow Cl^- + I_2$$

Such a heterolytic bond fission is not the only possible alternative, for Waters(132) has shown from theoretical calculations that in several typical "positive" halogen compounds the inductive and mesomeric effects of the essential organic substituents do little more than neutralise the incipient polarisation of the C-Halogen or N-Halogen links, and thus a homolytic fission of the type:-

$$R_1R_2R_3C\text{-Halogen} \longrightarrow R_1R_2R_3C\cdot + \cdot\text{Halogen}$$

is possible. Such a homolytic fission producing a neutral organic radical and an uncharged halogen atom may, in these compounds, require less energy than a dissociation of the heterolytic type. Several reactions of this type of compound in solvents of low polarity indicate the strong probability of homolytic fission occurring. Waters(128) has shown that N-chloroimides in suitable solvents are capable of attacking metals: thus solutions of dichloramine T. in benzene react when warmed with mercury to give a mixture of mercurous chloride and the mercuric salt of toluene p.sulphonamide. Such activity can be compared with that of free halogen atoms. Rust and Vaughan(133) have shown that α halogenated ketones can, like organic peroxides, catalyse the 'abnormal' addition of hydrogen bromide to olefines and Ziegler and co-workers(134) have shown that N-Halogen imides can substitute olefinic compounds in the allyl position in a way that is characteristic of free neutral radicals. From such evidence it seems highly probable that positive halogen compounds can, under suitable conditions, undergo homolytic fission to a free organic radical and an uncharged halogen atom, and should, in consequence, be capable of catalysing the autoxidation of tetralin by initiating reaction (3).

The catalytic effect of a series of N-Halogen imides on the autoxidation of tetralin was examined by the addition of 1 gm. of the substance under investigation to 30 mls of tetralin and measuring the rate of oxygen absorption in the static apparatus at 76°C. Results are shown in Table IX. It can be seen that in comparison with a sample of pure tetralin the initial rate of oxygen absorption in the presence of active halogenating agents such as N-bromo-succinimide was very high. This high rate of oxygen absorption gradually decreased as the homolytic fission of the halogen compound produced progressively fewer chain initiators. As with other catalysts of this type the level to which the oxygen absorption rate decreased when the production of chain initiators ceased was dependent upon the concentration of tetralin hydroperoxide then present in the system. Further examples of the catalysis of the autoxidation of tetralin by halogen compounds is given in Section VIII.

Table IX.

The Effect of N-Halogen Imides on the Autoxidation of Tetralin.

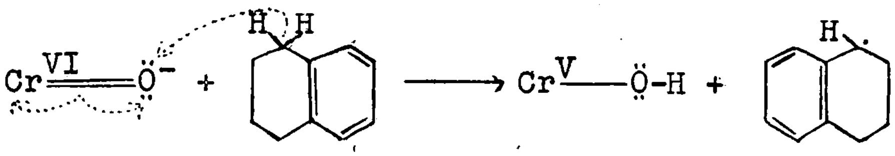
Substance Added	Oxygen Uptake mls/15 mins				Effect
	Time after addition				
	15 mins	30 mins	60 mins	120 mins	
Tetralin (Blank)	1.0	1.0	1.6	2.0	-
N-2:4-trichloro benzanilide	21.0	23.0	23.0	20.0	Catalysis
N-2:4:6-tetrachloro benzanilide	15.0	19.0	18.0	15.0	Catalysis
N-Bromo-succinimide	11.0	12.0	11.0	6.0	Catalysis
Bis-N-2:4:6:-tetra chloro-carbanilide	9.0	11.0	3.0	-	Catalysis
N-Bromo-phthalimide	5.0	3.0	1.0	-	Catalysis
N-Chloro-acetanilide	1.0	2.0	2.0	2.5	-
N-2:4:6-tetrachloro acetanilide	1.0	2.0	2.0	-	-

Oxidising and Dehydrogenating Agents.

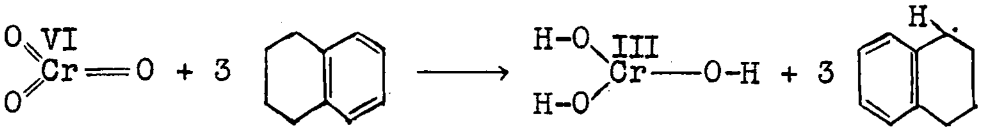
It has been suggested that hydrogen abstraction from the tetralin molecule with consequent formation of the tetralyl radical (equation 3) is the primary step in the autoxidation of tetralin. A series of oxidising agents which were of a characteristic dehydrogenating type were selected and their catalytic influence as chain initiators of the autoxidation investigated. Unless otherwise stated, the reactions were carried out in the static apparatus at 76°C. with 30 mls of tetralin.

Chromium Trioxide.

Farmer(38) has pointed out that chromic acid resembles oxygen and lead tetra-acetate in attacking at the α methylenic position in olefinic systems rather than at the double bond. Thus Whitmore and Pedlow(135) have shown that cyclohexene and 1 methyl cyclohexene are oxidised to carbonyl at the α methylenic group. The addition of a solution of 0.06 gm. chromium trioxide in 12 mls pure acetic acid to tetralin brought about an oxygen absorption which was both immediate and large. The rate of oxygen absorption decreased with time (Table X), and a small sludge of $Cr(OAc)_3$ was formed as the reaction proceeded. Waters(136) has suggested that the hydrogen abstraction may be pictured as a threefold repetition of the reaction:-

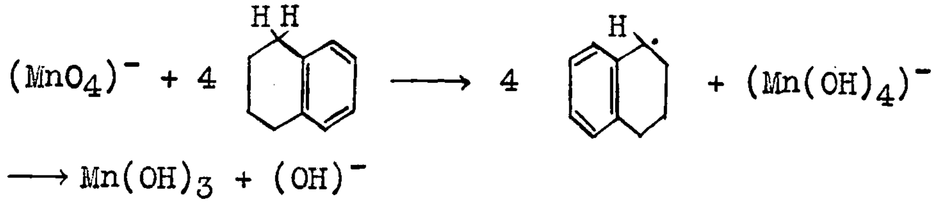


the overall reaction being:-



Potassium Permanganate.

A solution of potassium permanganate (0.05 gm.) in 15 mls pure acetic acid when added to tetralin brought about an immediate oxygen absorption (Table X). The absorption rate gradually decreased with time and a sludge of MnO_2 was formed as the reaction proceeded. Waters has suggested that a mechanism similar to that of the chromium trioxide reaction may occur:-



Periodic Acid.

Periodic acid has been shown to oxidise active methylene groups(137) and like lead tetra-acetate can split α glycols. The addition of 0.5 gm. of periodic acid in 10 mls of peroxide free dioxane to tetralin did not bring about an immediate increase in oxygen uptake, but, as can be seen from Table X, the rate gradually increased to a maximum value and then decreased again. The resultant solution was brown in colour and the decrease in uptake was probably accentuated by the inhibitory action of the decomposition products.

Osmic Acid.

Osmic acid is a catalyst for the hydroxylation of ethylenic bonds and functions by direct addition to give cyclic compounds(80) for which Waters(136) has suggested a single electron process of addition. The addition of a solution of 0.2 gm. of osmic acid in 10 mls of peroxide free dioxane to tetralin had no observable effect on the autoxidation. The osmic acid underwent immediate reduction to metallic osmium.

Selenium Dioxide.

Selenium dioxide attacks olefines, aldehydes and ketones at α methylenic groups and has been employed as a reagent for the hydroxylation of double bonds(138). Selenium dioxide (1 gm.) purified by sublimation was dissolved in 10 mls pure acetic acid and added to tetralin. Oxygen uptake was inhibited, the solution turned brown in colour, and red selenium was produced.

Quinones.

Quinones have been used as dehydrogenators of hydrocarbons(139, 140) at high temperatures and slowly convert tetralin to naphthalene, but the three investigated, benzoquinone, phenanthraquinone and chloranil, all inhibited the autoxidation of tetralin. The failure of quinones to catalyse the reaction is probably explained by the fact that Criegee(139) has observed that α tetralyl radicals unite with semiquinone radicals as an intermediate stage. Such a process would act as a chain breaker in the oxidation cycle and would account for the inhibition of the reaction.

Disulphides.

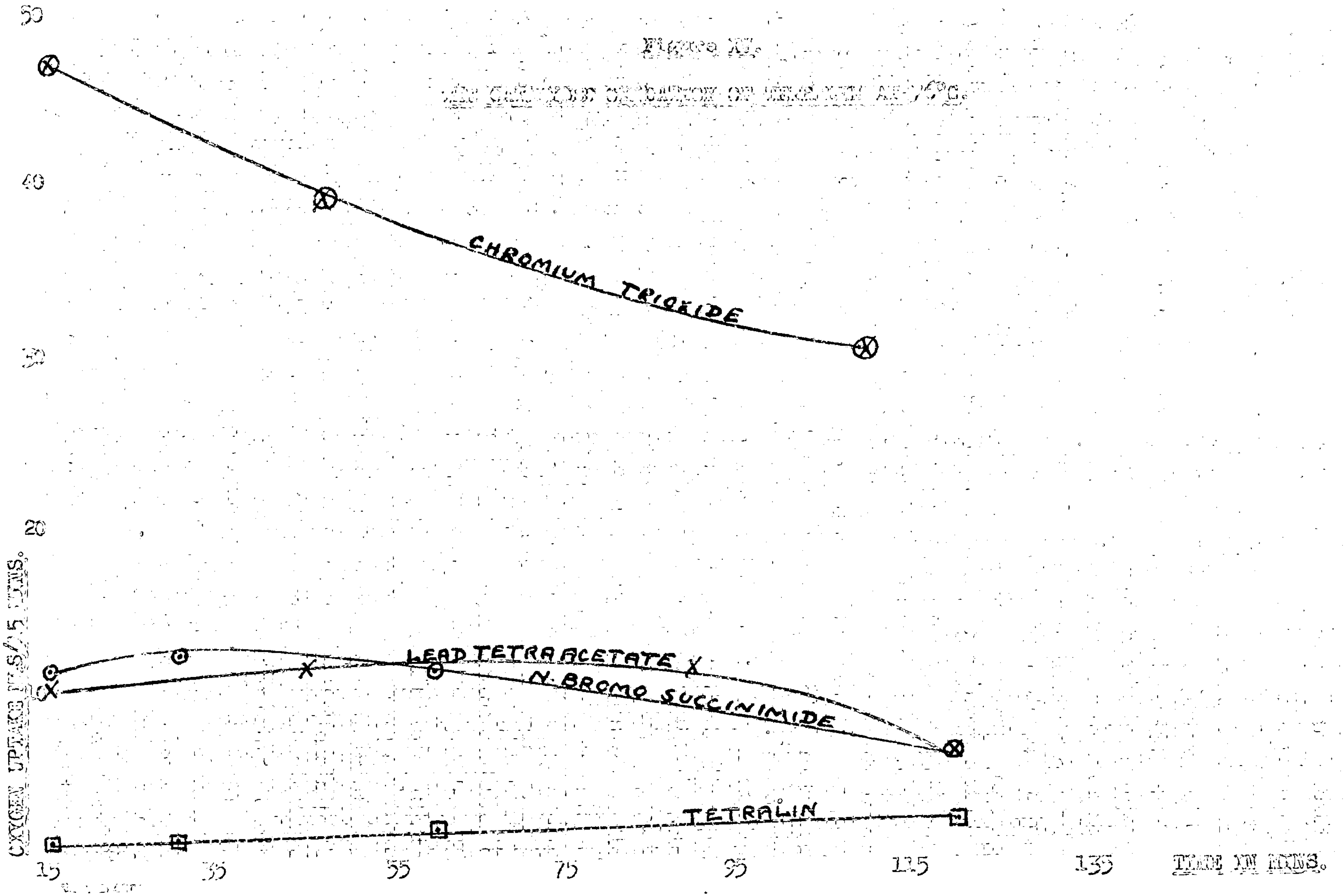
Disulphides have been shown to be effective dehydrogenating agents(141) and probably function by the production of mercaptide radicals:-

$$R\text{-}S\text{-}S\text{-}R \rightleftharpoons 2\ RS\cdot$$

The addition of 1 ml. quantities of iso-amyl disulphide and

Figure XI.

The Catalysed Oxidation of Tetralin at 70°C.



n-butyl disulphide to tetralin brought about an immediate absorption of oxygen, the rate of which gradually decreased with time, the reaction being finally inhibited. The decrease in oxygen absorption may be associated with a chain breaking reaction of the type:-

$$R\text{-}S\cdot + {>}CH\cdot \longrightarrow R\text{-}S\text{-}CH{<}$$

and ultimate inhibition may be related to either the presence of tetralol, which Denison and Condit(142) have shown is produced when disulphides react with tetralin hydroperoxide, or the production of thiols, which, as shown below, can function as inhibitors.

Mercapto Benzothiazole.

Mercapto benzothiazole has been used as an accelerator for rubber vulcanisation processes, but the addition of 1 gm completely inhibited the oxidation of tetralin. This supports the theory that the inhibition ultimately observed when disulphides are used as catalysts is connected with the presence of thiols in the system.

Selected examples of the catalysis of the autoxidation of tetralin are illustrated in Figure XV.

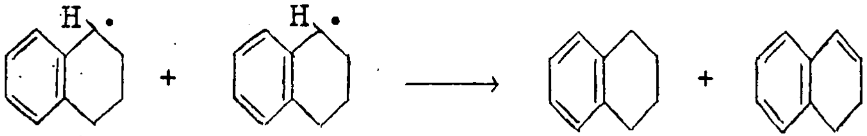
Table X.

The Effect of Dehydrogenating and Oxidising Agents on the Autoxidation of Tetralin.

Substance Added	Oxygen Uptake mls/15 mins							
	Time after addition							
	15 mins	30 mins	45 mins	60 mins	75 mins	90 mins	105 mins	180 mins
Tetralin (Blank)	0.5	0.7	0.9	1.1		1.2		1.8
Chromium Trioxide	47.0		39.0				30.0	16.0
Potassium Permanganate	37.0	26.1						11.5
Periodic Acid	0.5	3.0		7.8				6.9
Selenium Dioxide	No Uptake							
Osmic Acid	No Uptake							
Benzoquinone	0.2			0.2				
Phenanthroquinone	0.2			0.2				
Chloranil	0.2			0.2				
iso-Amyl Disulphide	2.4		1.6		0.6			
n-Butyl Disulphide	6.0	2.7		2.1		0.7		
Mercapto Benzothiazole	0.2			0.2				

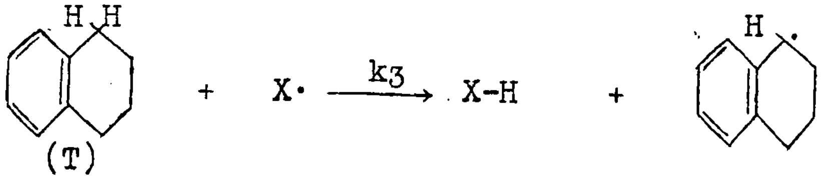
Discussion.

Phenyl pyridines have been produced by the reaction of the free phenyl radical with pyridine(143), but attempts to establish the presence of the tetralyl radical by adding pyridine to the autoxidising mixture in the hope of isolating a tetralyl pyridine were not successful. Sully(60) has provided strong evidence for the formation of hydrocarbon radicals of the type R_1 during oxidation processes by isolating 2:3 diphenyl butane, the dimerisation product of the phenyl ethyl radical, from the oxidation products of ethyl benzene. Attempts to isolate the corresponding dimer ditetralyl from the oxidation products of tetralin proved extremely difficult because of the complex nature of the mixture. A high boiling fraction was obtained which showed considerable fluorescence in ultra-violet light, but after repeated efforts to obtain a pure sample by chromatograph analysis (see Section VI) the product still contained a small percentage of oxygen (analysis C 89.0%, H 7.0%). Evidence was obtained, however, of the presence of 1:2 dihydronaphthalene (see Section VI), and it is probable that this compound was formed by disproportionation of the tetralyl radical:-



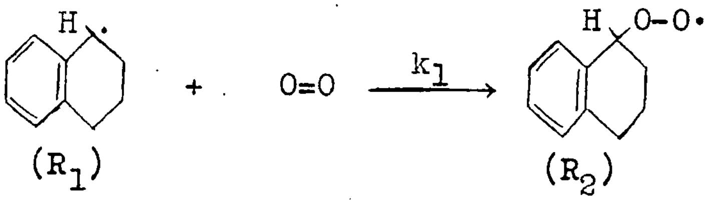
It is possible that attempts to isolate ditetralyl by distillation may have involved temperatures approaching the cracking point of the compound but no information is available on the subject.

The experimental evidence reviewed above demonstrates that free radicals and other dehydrogenating agents are excellent catalysts for the autoxidation of tetralin. This evidence supports the theory that the chain sequence involved in the initial phase of the autoxidation is of a free radical character, the first step in which is the formation of the tetralyl radical R_1:-

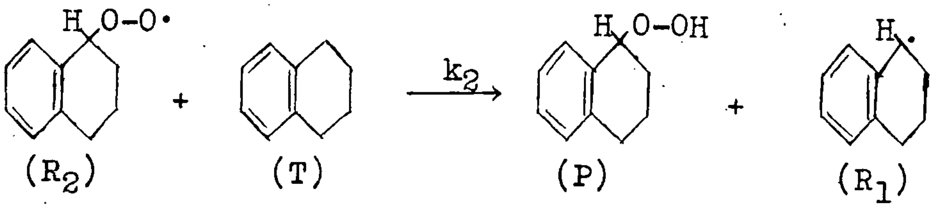


(4)

This radical may then react with oxygen to produce the peroxide radical (R_2) which, in its turn, may react with a molecule of hydrocarbon (T) to produce a molecule of hydroperoxide (P) and regenerate a tetralyl radical (R_1) which can initiate a further reaction cycle:-

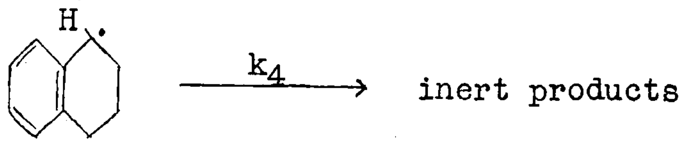


(5)



(6)

During the initial phase of the oxidation all the absorbed oxygen can be accounted for as hydroperoxide, and chain termination may therefore be represented by destruction of the tetralyl radical:-



(7)

The formation of the tetralyl radical in the initial step is facilitated by the activation of the methylene group because of its proximity to the aromatic ring, and the presence of the latter will also produce a resonance stabilisation of the radical.

Both chain propagation reactions 4 and 5 satisfy energy considerations. Basing calculations on the following bond strengths:-

C-H = 99 K.cal.(144)
C-O = 87 K.cal.(145)
O-O (in hydroperoxides) = 66 K.cal.(146)
O-O (in molecular oxygen) = 118 K.cal.
O-H = 110 K.cal.(147)

and ignoring the resonance energy of the radicals concerned, reaction 5 is exothermic (35 K.cal.) and reaction 6 is exothermic (11 K.cal.).

Considering the reaction sequence (equations 4, 5, 6 and 7) in the steady state:-

$$\frac{dR_1}{dt} = R_2Tk_2 + XTk_3 - R_1O_2k_1 - R_1k_4 = 0 \qquad (a)$$

$$\frac{dR_2}{dt} = R_1O_2k_1 - R_2Tk_2 = 0$$

Substituting $R_1O_2k_1 = R_2Tk_2$ in (a)

$$T_1k_4 = XTk_3$$

$$R_1 = \frac{XTk_3}{k_4}$$

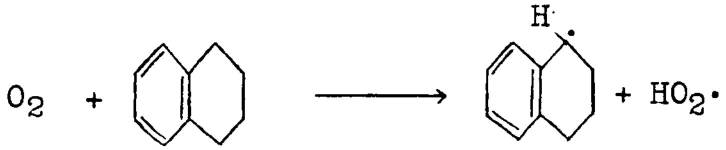
$$+\frac{dP}{dt} = -\frac{dO_2}{dt} = R_1 O_2 k_1$$

$$\text{Substituting } R_1 = XT\frac{k_3}{k_4}$$

$$+\frac{d(P)}{dt} = -\frac{d(O_2)}{dt} = k_1(O_2)\ \frac{k_3}{k_4}(T)(X)$$

The reaction rate is thus primarily dependent upon k_1 and the term inside the bracket is a function of chain starting and terminating processes, the nature of which, in the later stages of the reaction, is discussed in Section VII.

The catalyst X in equation 4 represents the agent bringing about the initial hydrogen abstraction (e.g. phenyl radicals), but in the normal thermal oxidation such catalysis is adventitious and probably arises from active spots on the reaction vessel. Initial production of tetralyl radicals by reaction of oxygen with the hydrocarbon



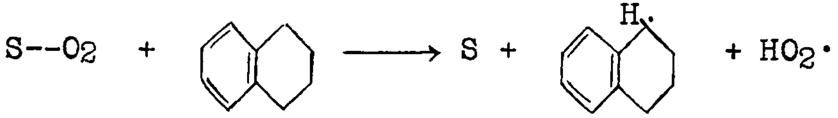
assuming approximate values of 14 K.cals.(148) and 15 K.cals.(146) for the resonance energies of the tetralyl and peroxide radicals would be endothermic having a heat of reaction of:-

$$\Delta H = 99 + 118 - 110 - 66 - 14 - 15 = 12 \text{ K.cal.}$$

Chain initiation by photo-activated oxygen molecules does not seem possible since oxygen does not absorb light greater than approximately 2,000 A°, and according to Bowen(149).

excitation of the oxygen molecule does not take place till 1,860 A°. Primary chain initiation may arise from the reaction of a hydrocarbon molecule with a molecule of oxygen activated by surface adsorption:-

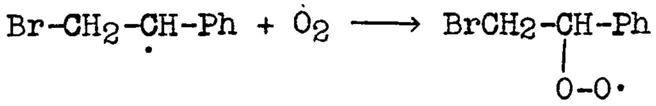
$$S + O_2 \longrightarrow S\text{--}O_2$$



It is doubtful, however, whether samples of tetralin are ever completely free from traces of the hydroperoxide, even although no reaction is obtained with potassium iodide, and the initiation of the first reaction chains is most probably a function of these sub-analytical quantities of hydroperoxide.

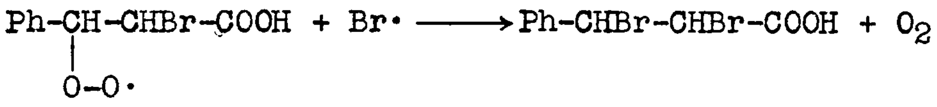
The observation of Bockemüller and Pfeuffer(150) that oxygen was absorbed during the reaction of unsaturated compounds such as styrene and allyl chloride with low concentrations of bromine in diffused light may be explained by a mechanism similar to that outlined above. It was found that oxygen was absorbed by the mixture only during the addition of bromine at the double bond and that a high percentage of the oxygen then absorbed was peroxidic. This may be explained by the following scheme assuming that halogenation takes place by an atomic mechanism:-

$$Br + CH_2 = CH\text{-}Ph \longrightarrow Br\text{-}CH_2\text{-}\underset{\bullet}{C}H\text{-}Ph$$



$$Br\text{-}CH_2\text{-}\underset{\bullet}{C}H\text{-}Ph + \dot{O}_2 \longrightarrow BrCH_2\text{-}\underset{\substack{|\\ O\text{-}O\cdot}}{C}H\text{-}Ph$$

The active $Br\text{-}CH_2\text{-}\underset{\bullet}{C}H\text{-}Ph$ radical is thus replaced by the less active peroxide radical which itself may initiate an autoxidation of the olefine. Brown and Daniels(151) have shown that the photo-bromination of cinnamic acid in carbon tetrachloride solution is retarded by the presence of small quantities of oxygen and that oxygen is absorbed during the initial bromine addition. These observations may be explained in the same manner as those of Bockemüller and Pfeuffer, and Waters(152) has suggested that retardation is probably a function of the peroxide radical produced, which can act as a chain breaker in the main bromination sequence:-



$$\underset{\text{O-O}\cdot}{\text{Ph-}\underset{|}{\text{CH}}\text{-CHBr-COOH}} + \text{Br}\cdot \longrightarrow \text{Ph-CHBr-CHBr-COOH} + O_2$$

The successful use of HBr as a catalyst of oxidation(153) processes may be similarly explained.

Weiss(154) suggested that free radical formation during oxidation was a two stage process involving electron transfer with the production of a radical cation, followed by proton transfer to produce a radical:-

$$\text{RH} \xrightarrow{\text{oxidation}} (\text{RH})^+ \ (+\ \text{electron})$$
$$(\text{RH})^+ \rightleftharpoons \text{R}\cdot + (\text{H})^+$$

There is, however, no fundamental difference between radical mechanisms and those involving single electron transfer because when the lifetime of the intermediate radical cation is short the reaction may be regarded as a simple hydrogen atom transfer. The ultimate product, the hydrocarbon radical, would be the same in each case and there would be no alteration in consequent reaction schemes. Radical cations have been chiefly encountered with diamines, azines, and similar compounds, but there is little evidence for their formation from simple hydrocarbons.

V. THE THERMAL DECOMPOSITION OF TETRALIN HYDROPEROXIDE.

(a) Kinetic Investigation.

Apparatus.

The decomposition of the hydroperoxide for kinetic purposes was carried out in the simple all glass apparatus shown in Figure XVIA.

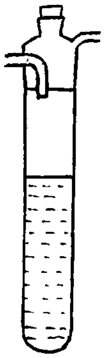


Figure XVIA.

It consisted of a reaction tube, capacity 50 mls., fitted with a glass cap stopper provided with a gas inlet and exit. A small standard joint which was stoppered when not in use was attached to the cap stopper and provided a means of sampling in an inert atmosphere. The reaction tube was heated by immersion in a vapour thermostat using trichlorethylene, water, toluene, n-butanol and ethyl benzene to obtain a suitable range of temperatures.

Method.

Approximately 1 gm. of pure crystalline tetralin hydroperoxide was accurately weighed into the reaction tube and dissolved in 15 mls. of peroxide free tetralin. The air in the reaction tube was displaced by nitrogen, the stopper inserted, and a very slow stream of nitrogen passed in to maintain the inert atmosphere. The tube was then immersed in the thermostat and the rate of hydroperoxide decomposition followed by periodic sampling by syringe pipette through joint 'A' and estimating the hydroperoxide content by the method described in Section II(b).

Experimental Results.

The results obtained are shown in Table XI.

For a first order reaction $k = \frac{2.303}{t} \log. \frac{a}{a-x}$

Where a = initial concentration, k = velocity constant,
x = decrease in the concentration after a time t.

Rearranging

$$t = \frac{2.303}{k} \log. a - \frac{2.303}{k} \log. (a - x)$$

Since $\frac{2.303}{k}$ log. a is constant then for a first order reaction the plot of t against log. (a - x) will be linear and the slope equal to $-\frac{2.303}{k}$.

For a second order reaction involving two molecules of the same reactant:-

$$k = \frac{1}{t} \; \frac{1}{a-x} - \frac{1}{a}$$

Rearranging

$$t = \frac{1}{k(a-x)} - \frac{1}{ka}$$

Table XI.

The Decomposition of Tetralin Hydroperoxide

Time from Start of decomposition in Hours	Weight of Sample (gms)	Titration (mls. 0.9891 $\frac{N}{10}$ $Na_2S_2O_3$)	Hydroperoxide/gm. Solution	Log. Hydroperoxide Concentration	Reciprocal of Hydroperoxide Concentration
At 88°C.					
0	0.7164	5.71	0.0646	-1.1895	15.47
2.33	0.8597	6.60	0.0622	-1.2059	16.06
4.50	0.8962	6.60	0.0597	-1.2239	16.74
6.33	0.9424	6.85	0.0589	-1.2296	16.96
8.33	1.0094	7.20	0.0579	-1.2375	17.28
10.33	0.8749	6.11	0.0566	-1.2469	17.66
12.33	0.9823	6.60	0.0545	-1.2637	18.35
At 100°C.		(mls. 0.9933 $\frac{N}{10}$ $Na_2S_2O_3$)			
0	0.7000	7.80	0.0907	-1.0422	11.03
2.00	0.7858	8.15	0.0845	-1.0733	11.84
4.41	0.8111	7.50	0.0753	-1.1232	13.28
6.75	0.7724	6.32	0.0666	-1.1763	15.01
8.50	0.7919	6.00	0.0617	-1.2097	16.21
10.33	0.7890	5.41	0.0558	-1.2531	17.91
12.50	0.8369	5.40	0.0525	-1.2798	19.03

(Cont'd)

Table XI. (Cont'd)

The Decomposition of Tetralin Hydroperoxide.

Time from Start of decomposition in Hours	Weight of Sample (gms)	Titration (mls. 0.9891 $\frac{N}{10}$ $Na_2S_2O_3$)	Hydroperoxide/gm. Solution	Log. Hydroperoxide Concentration	Reciprocal of Hydroperoxide Concentration
At 110°C.					
0	0.8986	7.10	0.0641	-1.1933	15.61
2.28	0.8918	5.71	0.0519	-1.2847	19.26
4.87	0.9607	4.80	0.0405	-1.3924	24.68
6.87	1.0082	4.21	0.0339	-1.4700	29.51
8.50	1.0113	3.71	0.0298	-1.5263	33.59
10.58	1.0177	3.01	0.0240	-1.6200	41.69
12.62	1.0380	2.60	0.0203	-1.6922	49.22
At 116°C.		(mls. 0.9933 $\frac{N}{10}$ $Na_2S_2O_3$)			
0	0.8129	6.42	0.0643	-1.1918	15.55
2.00	0.8425	4.85	0.0468	-1.3293	21.34
4.08	0.8671	3.65	0.0339	-1.4694	29.47
6.17	0.9618	2.99	0.0253	-1.5966	39.50
8.75	1.0482	2.27	0.0177	-1.7526	56.57
10.83	1.0728	1.71	0.0130	-1.8868	77.05
12.25	1.0811	1.39	0.0105	-1.9784	95.15

(Cont'd)

Table XI. (Cont'd)

The Decomposition of Tetralin Hydroperoxide.

Time from Start of decomposition in Hours	Weight of Sample (gms)	Titration (mls. 0.9933 $\frac{N}{50}$ $Na_2S_2O_3$)	Hydroperoxide/gm. Solution	Log. Hydroperoxide Concentration	Reciprocal of Hydroperoxide Concentration
At 135°C.					
0	0.7607	28.4	0.0608	-1.2161	16.44
0.70	0.8775	20.3	0.0377	-1.4240	26.55
1.40	0.8980	12.7	0.0230	-1.6377	43.42
2.92	1.1275	5.4	0.0089	-2.1076	128.10
3.92	2.3172	5.4	0.0038	-2.4207	263.40

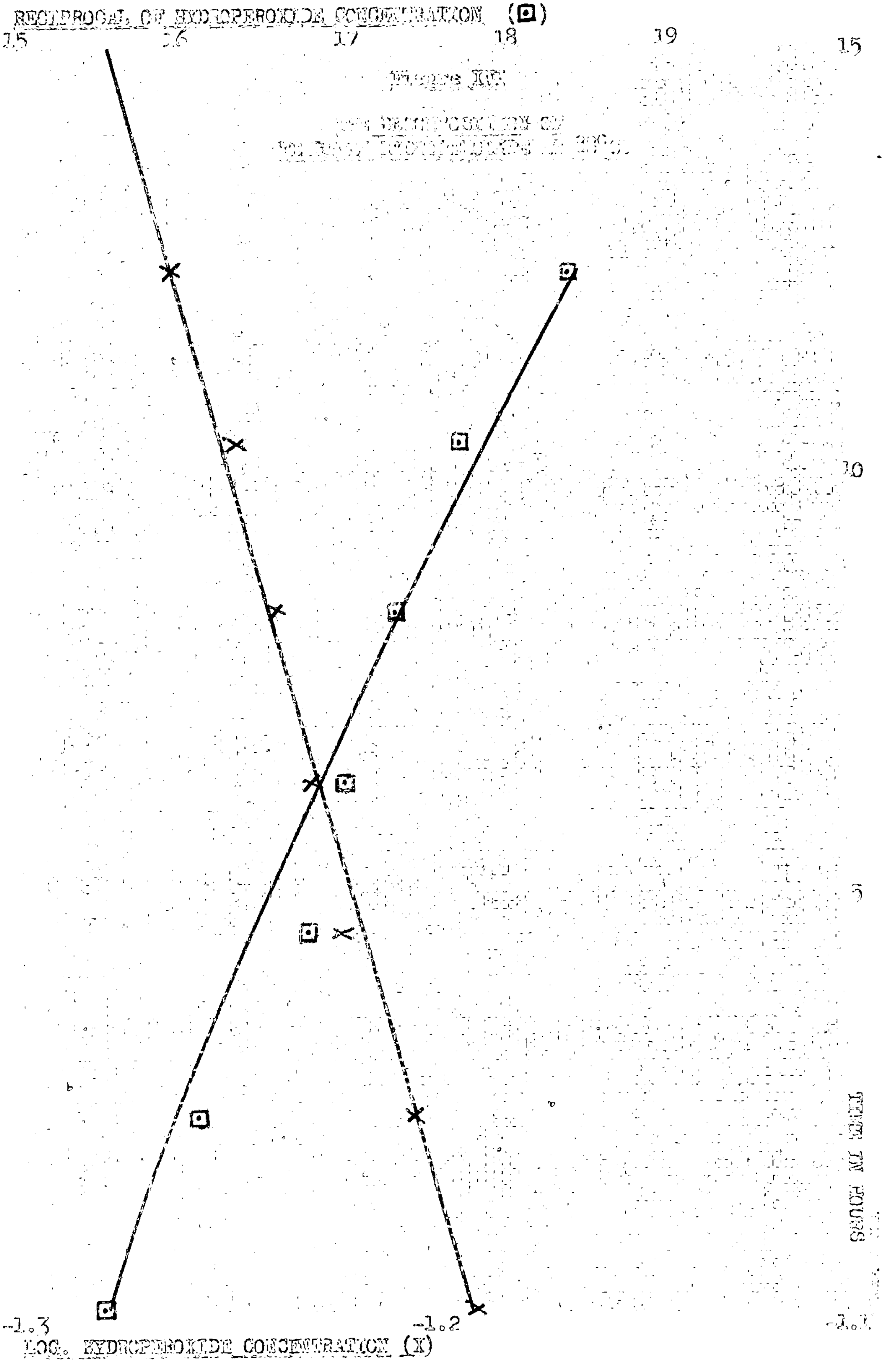


Figure [illegible]

THE DECOMPOSITION OF
[illegible] HYDROPEROXIDE AT 30°C.

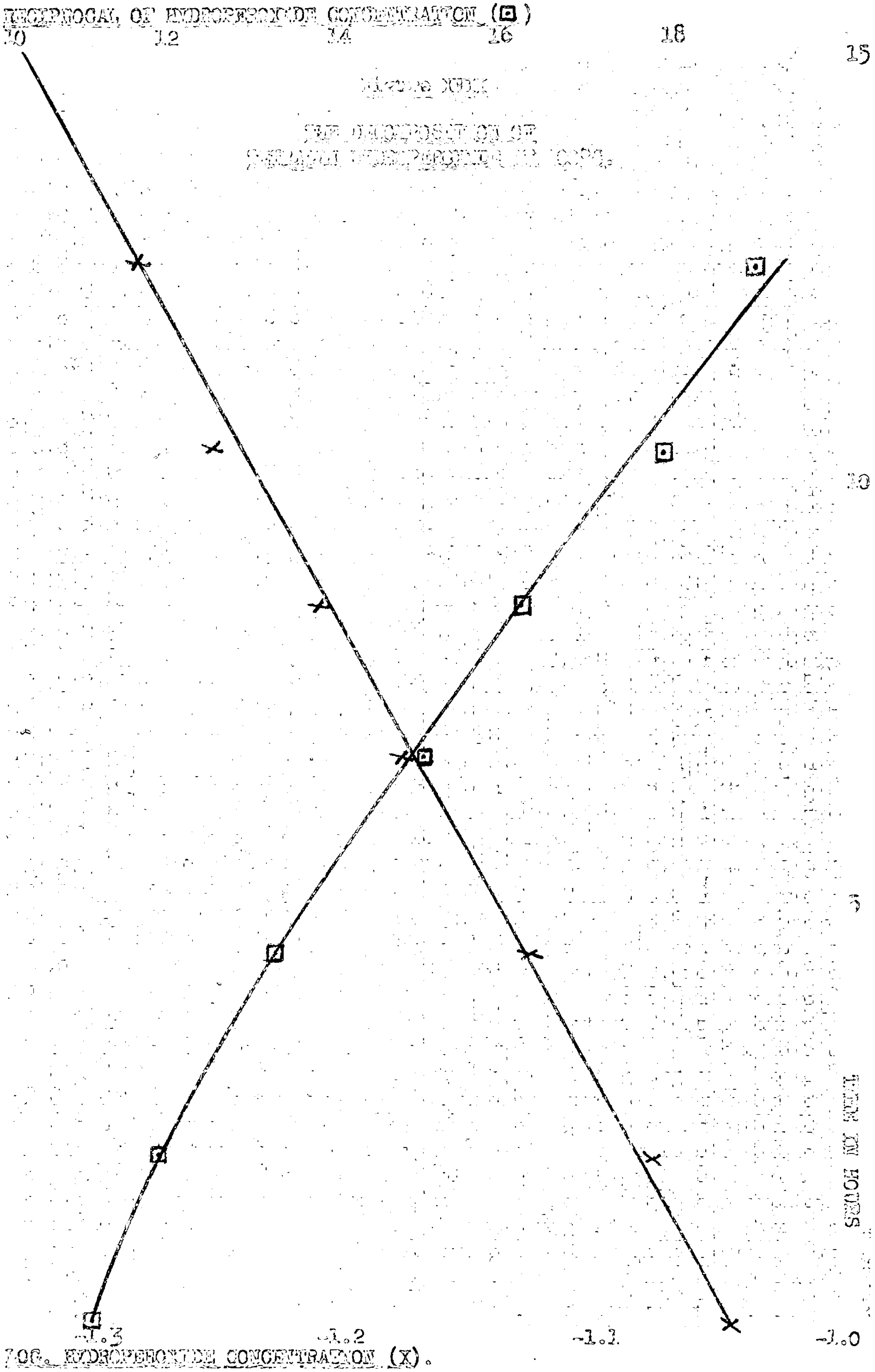


Figure XVII

THE DECOMPOSITION OF
TETRALIN HYDROPEROXIDE IN CCl4.

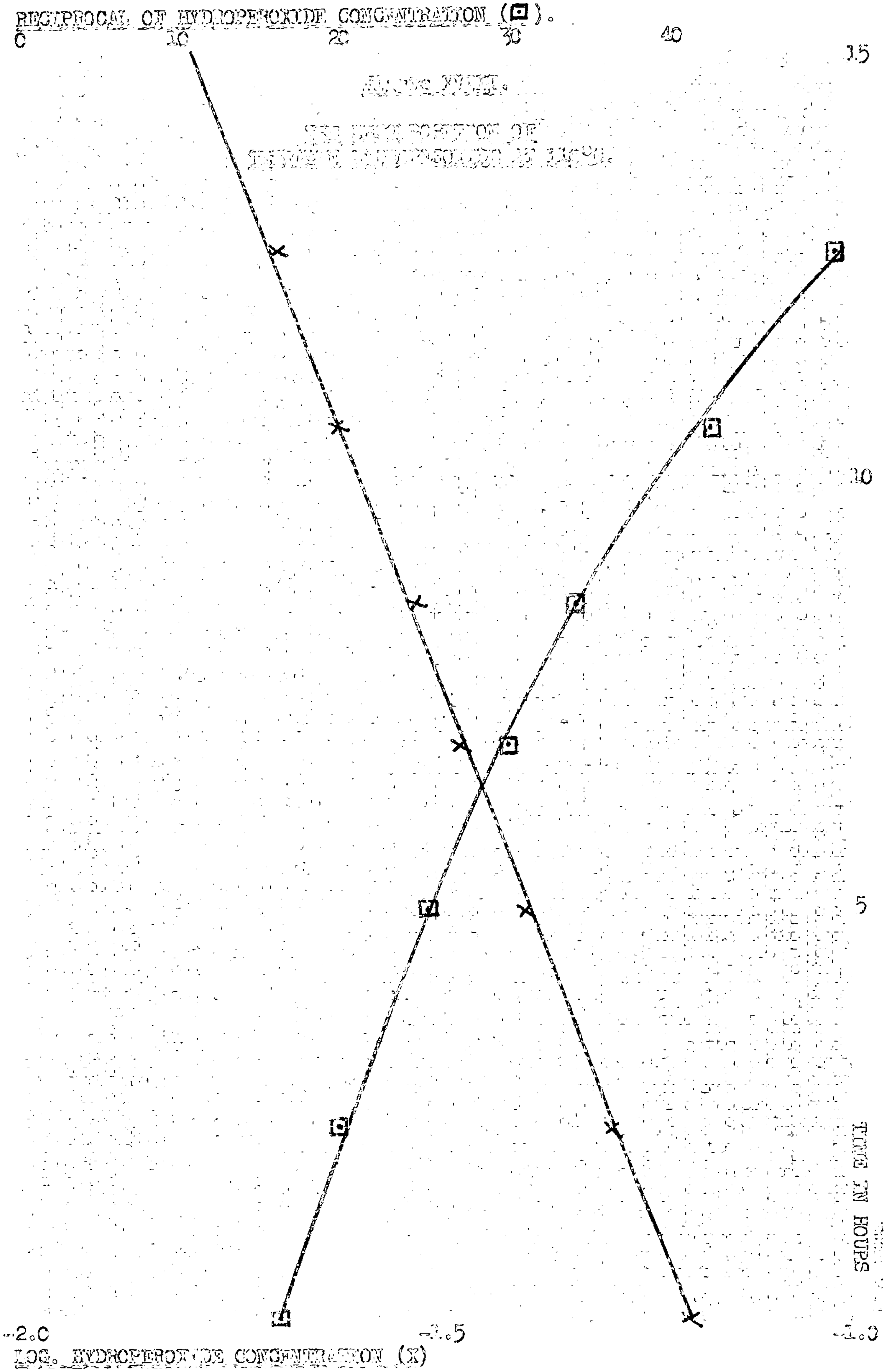


FIGURE XVIII.

THE DECOMPOSITION OF
[illegible] HYDROPEROXIDE IN [illegible].

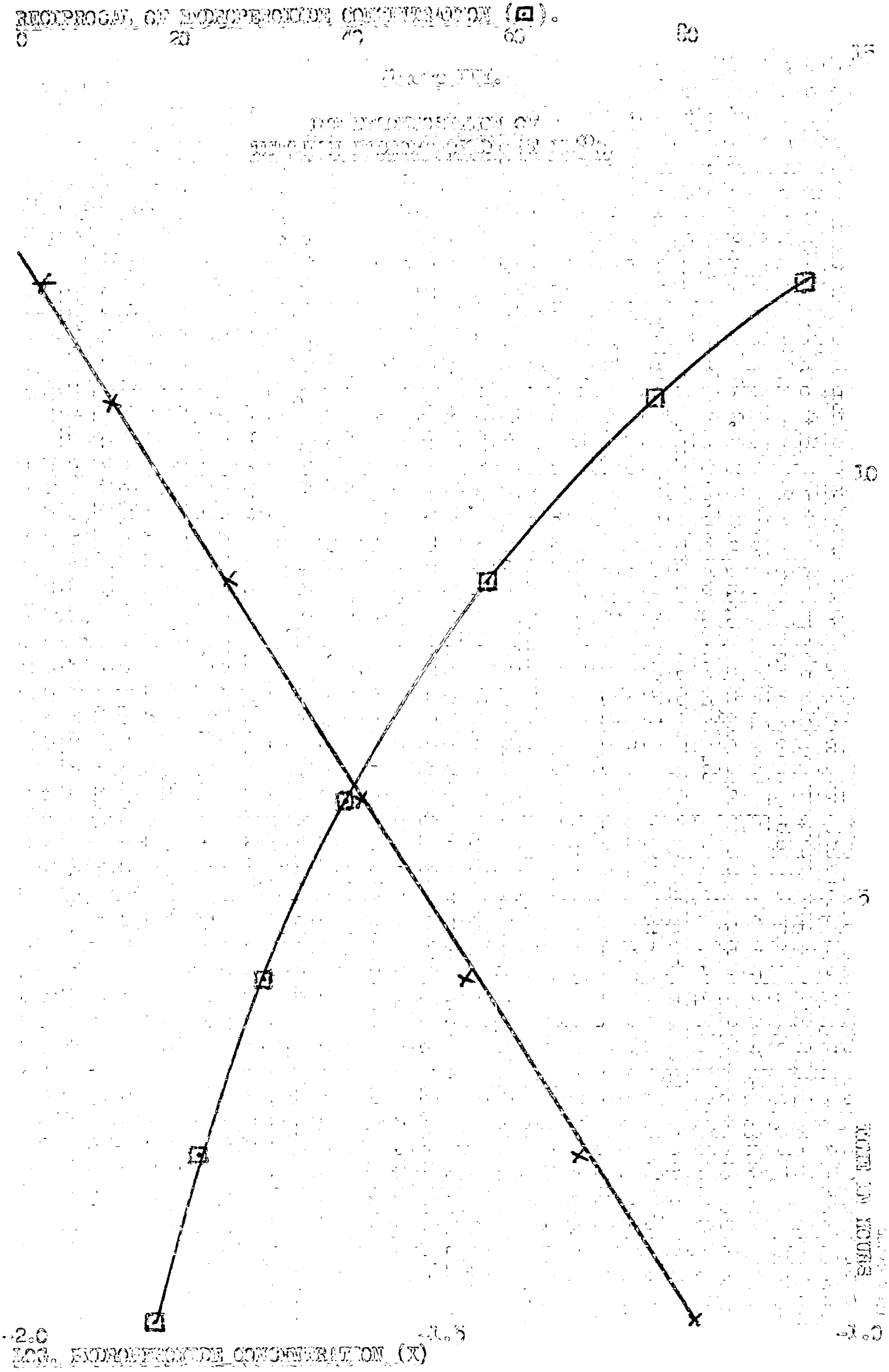
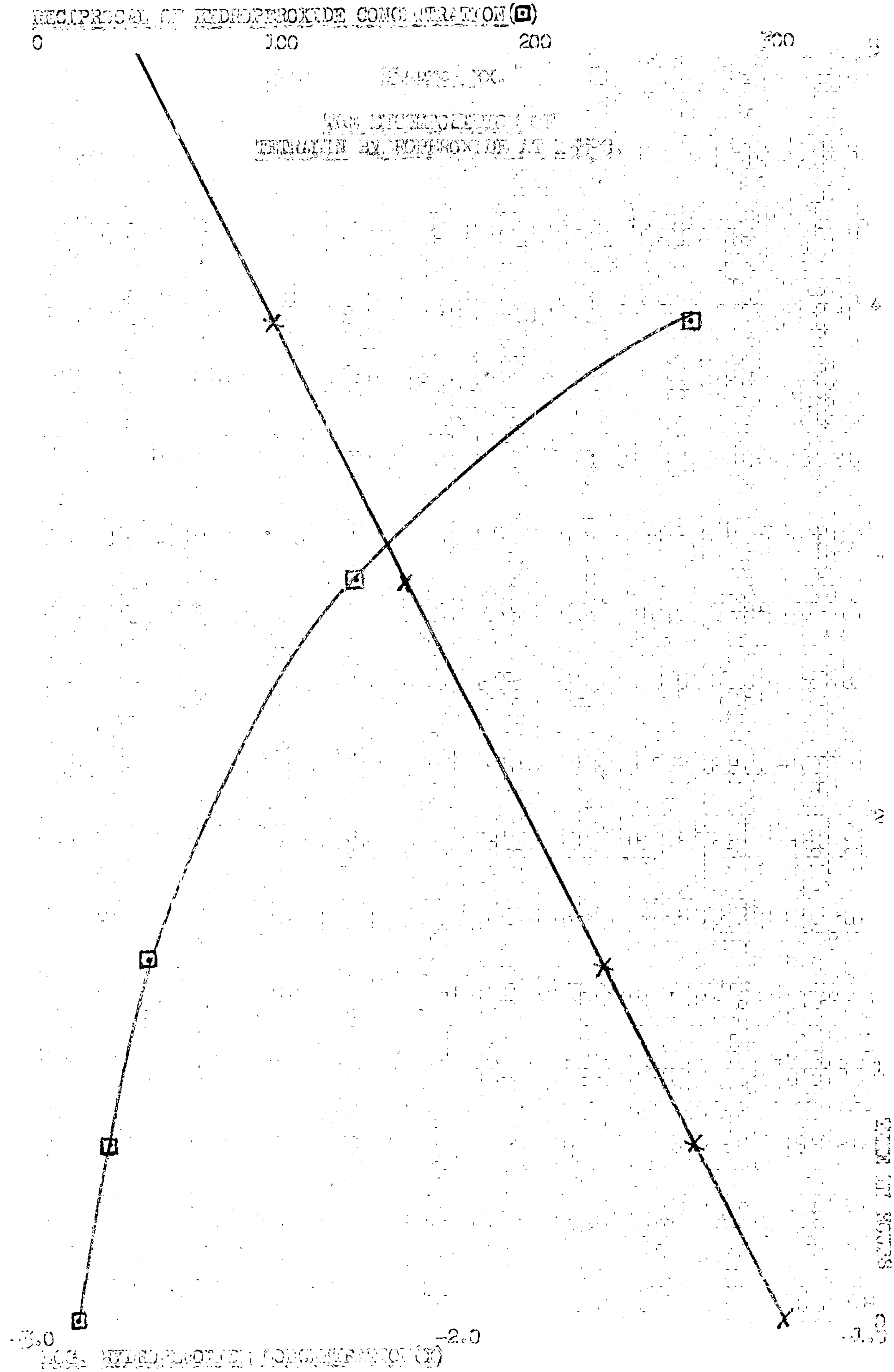


Figure XII.

THE DECOMPOSITION OF
[illegible]


RECIPROCAL OF HYDROPEROXIDE CONCENTRATION (⊡)
0
100
200
300
FIGURE XX.
THE DECOMPOSITION OF
TETRALIN HYDROPEROXIDE AT [illegible]°C.
6
4
2
0
TIME IN HOURS
-3.0
-2.0
-1.0
LOG. HYDROPEROXIDE CONCENTRATION (X)

Hence, for a second order reaction the plot of t against $\frac{1}{a - x}$ is linear and the slope = $\frac{-1}{k}$.

Columns 5 and 6 in Table XI show values for the logarithm of the residual hydroperoxide concentration (log. (a - x)) and the reciprocal of the residual hydroperoxide concentration $\frac{1}{(a - x)}$.

Figures XVI, XVII, XVIII, XIX and XX show the plot of time against the logarithm of the residual hydroperoxide concentration and the reciprocal of the residual hydroperoxide concentration at the varying temperatures. It can be seen that in each case the variation of the logarithm of the residual peroxide concentration with time is linear and the decomposition is, therefore, of the first order. The slope of the graph for the first order reaction is $-\frac{2.303}{k}$ and values of k, the velocity constant of the reaction, obtained from Figures XVI, XVII, XVIII, XIX and XX are shown in Table XII below.

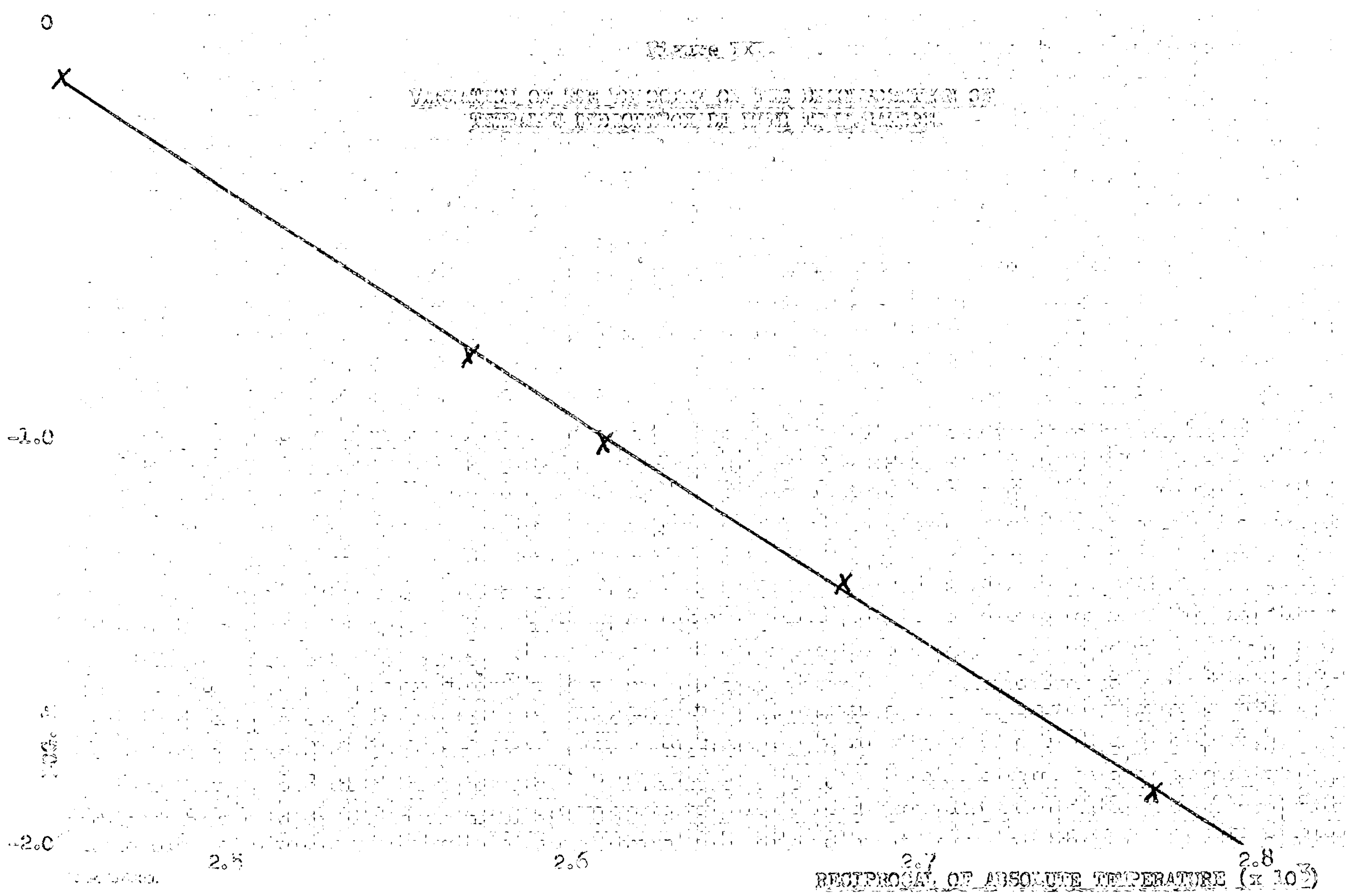
Table XII.

Variation of the Velocity Constant of the Decomposition of Tetralin Hydroperoxide with Temperature.

Temperature of Decomposition	k
°C.	
88	.0133
100	.0435
110	.0921
116	.1498
135	.7093

Figure IX.

VARIATION OF THE VELOCITY OF THE DECOMPOSITION OF [illegible] HYDROPEROXIDE WITH TEMPERATURE



If the decomposition obeys the Arrhenius equation ($\ln k = \frac{-E}{RT}$ + constant) then a plot of log. k against the reciprocal of the absolute temperature of the reaction should be a straight line. The results in Table XIII are illustrated in Figure XXI.

Table XIII.

Temperature °C.	Reciprocal of Absolute Temperature	log. k
88	.00277	-1.8761
100	.00268	-1.3615
110	.00261	-1.0357
116	.00257	-0.8245
135	.00245	-0.1492

These results show that the decomposition of tetralin hydroperoxide does obey the Arrhenius equation.

Since $\log. k = \frac{-E}{2.303\ RT} + C.$ then the slope of the

$$\text{graph} = \frac{-E}{2.303\ R} = \frac{-1.84}{.3450 \times 10^{-3}}$$

The activation energy of the decomposition (E) is

therefore $\frac{1.84 \times 2.303\ R}{.3450 \times 10^{-3}}$ = 24.40 K.cals/mol.

Solvent Effect.

Ivanov et al(85) reported that they had observed a solvent effect when studying the decomposition of tetralin hydroperoxide, the decomposition rate being higher in tetralin than in decalin. Confirmation of this solvent effect was obtained by investigating the decomposition of the hydroperoxide in substances other than tetralin. The wide range of variation of the rate of decomposition in different solvents is shown in Table XIV.

Table XIV.

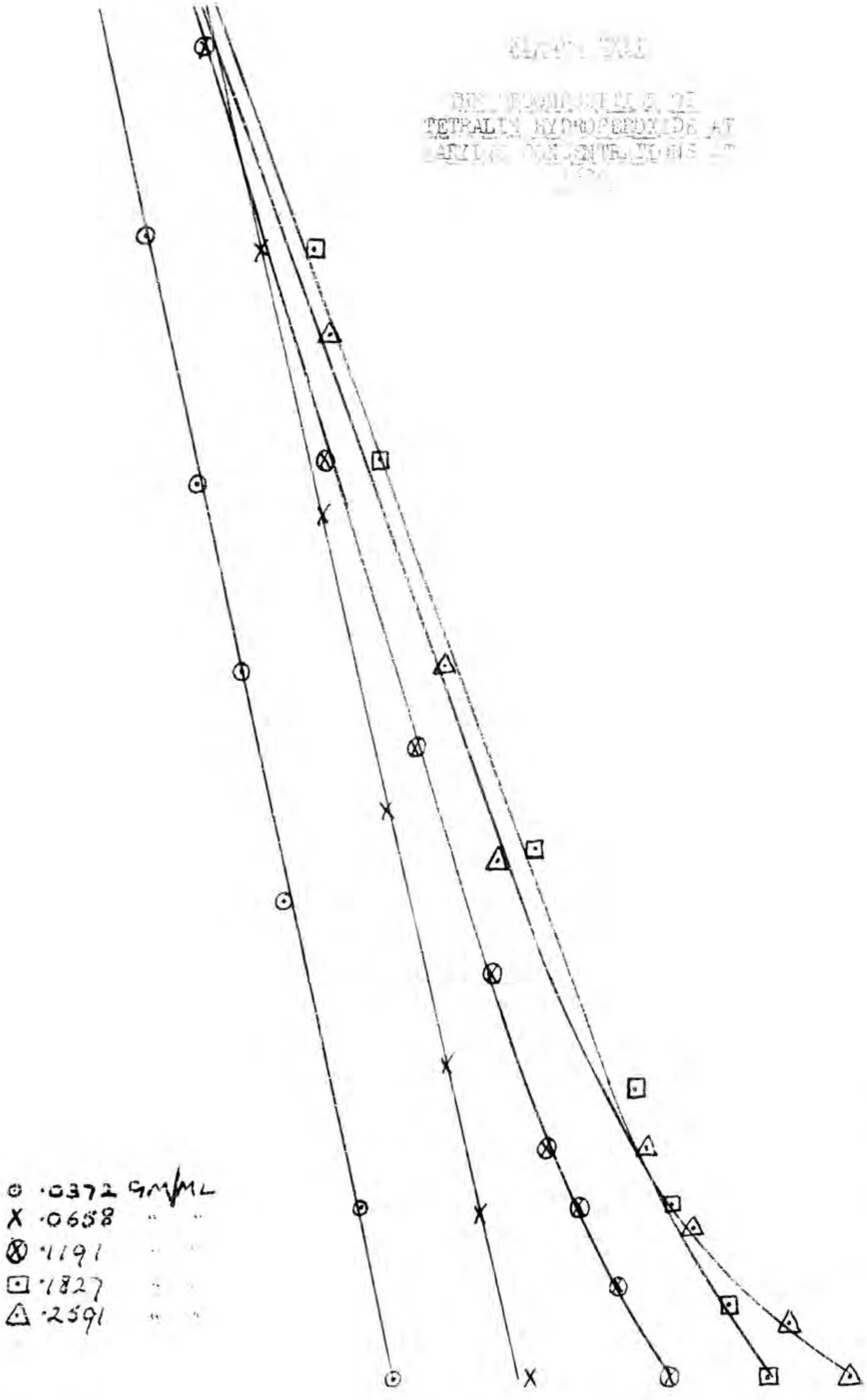
Solvent Effect on the Rate of Decomposition of Tetralin Hydroperoxide.

Solvent	% Hydroperoxide Decomposed after 1 hour at 116°C.
Tetralin	10
Chlorbenzene	10
Dichlorbenzene	30
Cyclohexanone	41
Cyclohexanol	78
Chlornaphthalene	100

Nozaki and Bartlett(155) have observed a similar wide variation for the rate of decomposition of benzoyl peroxide in a variety of solvents and have suggested that the explanation is dependent upon the further reaction of free radicals, produced during the decomposition, with the solvent. It appeared, therefore, that the decomposition of tetralin hydroperoxide was more complex than was apparent from the

GRAPH XXII

THE DECOMPOSITION OF
TETRALIN HYDROPEROXIDE AT
VARYING CONCENTRATIONS IN
[illegible]



preliminary kinetic results, and this complexity was further illustrated when the kinetics of the decomposition of solutions of varying concentrations of the hydroperoxide were investigated.

Concentration Effect.

The results obtained from an investigation of the decomposition of the hydroperoxide at varying concentrations are shown in Table XV and Figure XXII.

Table XV.

The Effect of Concentration on the Rate of Decomposition of Tetralin Hydroperoxide at 116°C.

Time in mins. from start of Decomposition	Hydroperoxide gm./ml. solution	Log. of Residual Hydroperoxide Concentration	Reciprocal of Residual Hydroperoxide Concentration
Concentration of Hydroperoxide .0372 gm./ml.			
0	.0372	-1.4295	26.08
65	.0317	-1.4989	31.54
175	.0235	-1.6289	42.55
257	.0193	-1.7144	51.81
327	.0161	-1.7932	62.12
415	.0133	-1.8761	75.18

(Cont'd)

Table XV. (Cont'd).

The Effect of Concentration on the Rate of Decomposition of Tetralin Hydroperoxide at 116°C.

Time in mins. from start of Decomposition	Hydroperoxide gm./ml. solution	Log. of Residual Hydroperoxide Concentration	Reciprocal of Residual Hydroperoxide Concentration
Concentration of Hydroperoxide .0658 gm./ml.			
0	.0658	-1.1818	15.20
60	.0541	-1.2668	18.48
115	.0467	-1.3307	21.41
205	.0389	-1.4101	25.71
315	.0271	-1.5670	36.90
410	.0220	-1.6556	45.25
Concentration of Hydroperoxide .1191 gm./ml.			
0	.1191	-0.9241	8.40
30	.0922	-1.0353	10.85
65	.0820	-1.0862	12.20
85	.0710	-1.1487	14.08
147	.0560	-1.2518	17.85
232	.0400	-1.3979	25.00
335	.0275	-1.5607	36.37
485	.0160	-1.7959	62.50

(Cont'd)

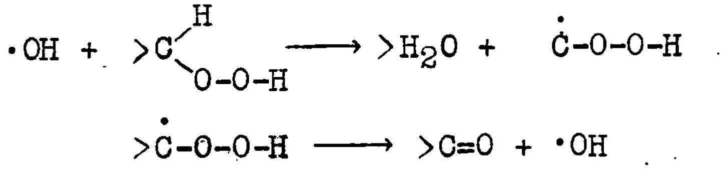
Table XV. (Cont'd)

The Effect of Concentration on the Rate of Decomposition of Tetralin Hydroperoxide at 116°C.

Time in mins. from start of Decomposition	Hydroperoxide gm./ml. solution	Log. of Residual Hydroperoxide Concentration	Reciprocal of Residual Hydroperoxide Concentration
Concentration of Hydroperoxide .1827 gm./ml.			
0	.1827	-0.7383	5.47
27	.1508	-0.8217	6.63
65	.1203	-0.9198	8.31
107	.0978	-1.0097	10.23
194	.0601	-1.2211	16.63
265	.0463	-1.3344	21.60
335	.0353	-1.4522	28.32
412	.0268	-1.5719	37.32
Concentration of Hydroperoxide .2591 gm./ml.			
0	.2591	-0.5865	3.86
20	.1985	-0.7022	5.04
56	.1345	-0.8713	7.43
85	.1082	-0.9658	9.24
190	.0590	-1.2291	16.94
260	.0467	-1.3307	21.41
380	.0283	-1.5482	35.34
515	.0160	-1.7959	62.50

The decomposition was of first order up to a concentration of 0.12 gm./ml. Thereafter there was appreciable divergency from the linear relationship required for a first order reaction and higher rates of decomposition were obtained.

The rate of decomposition of benzoyl peroxide has been shown to exhibit variation with differing concentrations of solution(156). Nozaki and Bartlett have suggested that this variation can be explained by assuming that free radicals produced during the decomposition of the peroxide can induce further decomposition. They obtained evidence supporting this theory by showing that hexaphenyl ethane, pentaphenyl ethane and tetraphenyl hydrazine all greatly increased the rate of decomposition of benzoyl peroxide solutions. A similar explanation may be applicable to the differing rates of the decomposition of tetralin hydroperoxide at varying concentrations. Thus, for example, hydroxyl radicals if produced during the decomposition may attack the hydroperoxide molecule and so induce an increase in the rate of decomposition:-



$$\cdot OH + {>}C\begin{matrix} H \\ O{-}O{-}H \end{matrix} \longrightarrow {>}H_2O + \dot{C}{-}O{-}O{-}H$$

$$>\dot{C}{-}O{-}O{-}H \longrightarrow >C{=}O + \cdot OH$$

The frequency of such a reaction would be dependent upon both the concentration of the solution and the extent to which the solvent cage effect(157) functioned (see Section V). The solvent and concentration effects indicated that the decomposition of tetralin hydroperoxide was not a simple molecular reaction, but involved the intermediate formation of free radicals.

(b) Products of the Thermal Decomposition of Tetralin Hydroperoxide.

It has been assumed by many workers that on decomposition tetralin hydroperoxide forms α tetralone in almost quantitative yield. George and Robertson(95) assumed that the decomposition was a simple dehydration and made no effort to investigate the nature of the products of the reaction. Medvedev and Podyapolskaya(93) made an unsuccessful search for alcoholic compounds among the oxidation products, and criticism has already been made of the method they employed. An examination of the products of the thermal oxidation of tetralin (see Section VI) showed that α tetralol and other hydroxy compounds were present in appreciable quantities, and it was therefore decided to carry out quantitative estimations of the principle products of the decomposition.

Materials.

Tetralin Hydroperoxide

As described in Section II(a).

α Tetralone

The method adopted for the preparation of tetralone was, with slight modifications, that of Organic

Syntheses, 20, 94. Tetralin was oxidised under conditions identical to those for the preparation of the hydroperoxide, and then, after cooling, the oxidised hydrocarbon was treated with 2N sodium hydroxide with vigorous shaking. The solution was slowly warmed to 60°C. (cooling was found necessary to slow down the rate of reaction once it was initiated). When the reaction was complete the solution was cooled and the excess sodium hydroxide almost completely neutralised with 6N sulphuric acid. After separating the tetralin layer, it was washed with dilute sulphuric acid and, after reseparating, was dried with anhydrous sodium sulphate (calcium chloride could not be used for the drying of αtetralone because it reacted to give a complex, cf. Medvedev and Podyapolskaya). The product was fractionally distilled and the fraction boiling at $105\text{-}107^{\circ}\mathrm{C.}_{2\ \mathrm{mm.}}$ collected. Analysis of this fraction showed that it was not 100% αtetralone but probably contained αtetralol which boils at the same temperature. A further purification by the method of Kipping and Hill(158) was, therefore, carried out. This involved the preparation of the semi-carbazone by the usual technique, recrystallising it from alcohol, and regenerating αtetralone by treatment with 50% hydrochloric acid. The αtetralone was then steam distilled from the mixture and, after ether extraction, drying, and removing the solvent, was once more distilled under reduced pressure, B.P. $99^{\circ}\mathrm{C.}_{.9\ \mathrm{mm.}}$

∝Tetralol.

∝Tetralol was prepared by the method of Hock and Lang(23). 21 Gms. of pure tetralin hydroperoxide were vigorously shaken with a solution of 50 gms. of sodium sulphite heptahydrate in 250 mls. of water. The oily layer of ∝tetralol which was produced was extracted with ether, and after drying and removing the solvent, the residual liquid was fractionally distilled at reduced pressure. Finally, in order to remove traces of ∝tetralone the product was redistilled at reduced pressure ($B.P._{.9mm.}$ 99°C.) from a little 2:4 dinitro phenyl hydrazine.

Analytical Methods.

Estimation of Tetralin Hydroperoxide.

As described in Section II(b).

Estimation of ∝Tetralone.

A survey was made of the methods employed for ketone estimation, and it appeared most probable that a gravimetric estimation of ∝tetralone as its 2:4 dinitro phenyl hydrazone or a volumetric estimation by oximation would prove satisfactory.

Estimation as 2:4 Dinitro Phenyl Hydrazone.

The 2:4 dinitro phenyl hydrazone of ∝tetralone possesses a very low solubility in water, and since it is quite stable to heat at 100°C. may be dried without danger of decomposition. The precipitant, 2:4 dinitro phenyl hydrazine, was prepared as a saturated solution in 2N hydrochloric acid.

The rate of filtration varied appreciably with the solvent used and a 1:1 mixture of alcohol and water was found to give a friable precipitate capable of easy filtration.

The sample was weighed into a stoppered flask, dissolved in 30 mls. of solvent, and the required quantity of precipitant added. After vigorous shaking, the solution was allowed to stand for one hour and was then filtered through a sintered glass crucible. The precipitate was washed free of excess precipitant with N hydrochloric acid and finally washed chloride free with distilled water. The product was dried at 100°C. and weighed.

1 gm. dinitro phenyl hydrazone $\equiv$ 0.4478 gms α tetralone. This method was found to be both accurate and of reasonable speed. An average of three estimations with samples of pure α tetralone gave a result which was 99.3% of the theoretical value.

The use of this method was very much restricted by the fact that the presence of tetralin rendered it inaccurate. In the presence of tetralin the dinitro phenyl hydrazone formed a red oil, and even when the alcohol ratio in the solvent was varied, difficulty was experienced in filtration and loss occurred in the filtrate. The method could not be used in the presence of tetralin hydroperoxide because side reactions ensued and results were unreliable.

Estimation by Oximation.

Estimation of a ketone by oximation involves treatment with hydroxylamine hydrochloride in a suitable solvent and estimation of the liberated hydrochloric acid by titration with standard alkali. It was found preferable to work in methanolic solution because this reduced the time required for complete oximation and eliminated end point difficulties caused by turbidity. Hydroxylamine hydrochloride was, therefore, prepared as a 10% solution in 80% alcohol, and the standard alkali prepared as a methanolic solution. Oximation at room temperature gave results which were only 75% of the theoretical value, and it was found necessary to heat the reaction mixture under reflux on a water bath for two hours in order to obtain quantitative results. A choice of indicator caused some difficulty, but both bromophenol blue, pH 3.0-3.6, and dimethyl yellow, pH 2.8-4.6, gave end points which were sufficiently sharp to give reproducible results.

Twenty mls. of solvent were added to each of two conical flasks, followed by the requisite amount of alcoholic hydroxylamine hydrochloride. The solutions were then adjusted to neutrality to dimethyl yellow indicator (0.1% solution in methyl alcohol) with $\frac{N}{10}$ alcoholic sodium hydroxide. The sample to be analysed was added to one flask and both it and the blank were heated under reflux on a water bath for two hours. After cooling, both samples were titrated to neutrality with $\frac{N}{10}$ alcoholic sodium hydroxide,

$$1 \text{ ml. } \frac{N}{10} \text{ NaOH} \equiv 0.0146 \text{ gm. } \alpha \text{tetralone.}$$

The method gave excellent results with samples of pure αtetralone (98.5% of the theoretical value).

Hydroxylamine hydrochloride is attacked by tetralin hydroperoxide and, in consequence, in the presence of the latter, the above method could not be used because of the unreliability of the results obtained. Oxidation products were often dark in colour, and this prevented the use of indicators because of the extreme difficulty of end point determination. The following modification was adopted for use with such solutions. The procedure was repeated until the period of refluxing was completed. The blank solution was transferred to a beaker, a glass electrode inserted, the system connected to a Calomel half cell and a Cambridge pH meter, and the pH thus determined. This process was then repeated with the sample solution and $\frac{N}{10}$ alcoholic sodium hydroxide added until the pH was identical to that of the blank (approximately 3.5).

Estimation of Alcohol.

The standard acetylation method was adopted for alcohol estimation. The sample was refluxed on a water bath with a suitable quantity of acetic anhydride in anhydrous pyridine. A blank estimation with identical quantities of reagents was subjected to the same treatment. After two hours refluxing the samples were well diluted with distilled water and titrated with $\frac{N}{5}$ alcoholic sodium hydroxide using phenolphthalein as indicator. Allowance was made for the free acid present in the sample.

$$1 \text{ ml. } \frac{N}{5} \text{ NaOH} \equiv 0.0296 \text{ gms. } \alpha \text{ tetralol}$$

The method gave excellent results with samples of pure α tetralol (97% of the theoretical value).

Analysis of Tetralol-Tetralone Mixtures.

A synthetic mixture comprising 50% pure α tetralone and 50% pure α tetralol gave results which were 97% of the theoretical value for the ketone and 97% of the theoretical value for the alcohol.

Estimation of Free Acids.

Free acids were estimated by direct titration with methanolic sodium hydroxide.

Estimation of Saponifiable Materials.

An estimation of saponifiable materials (esters, lactones, etc.) was carried out by refluxing the sample for analysis with methanolic sodium hydroxide for two hours and then titrating the excess alkali with $\frac{N}{10}$ hydrochloric acid, allowance being made for free acids present in the sample. End point determinations were too difficult to determine with indicators-and the electrometric method was used.

Estimation of Water.

The standard method for determination of water using Fischer's reagent could not be employed because of the dark brown colour of the solutions to be analysed and alternative methods were investigated. R.P. Bell[159] developed a method which utilised the reaction of αnaphthoxy dichlorophosphine with water to produce hydrogen chloride:-

$$C_{10}H_7\cdot O\cdot PCl_2 + 2H_2O \longrightarrow C_{10}H_7\cdot O\cdot P(OH)_2 + 2HCl$$

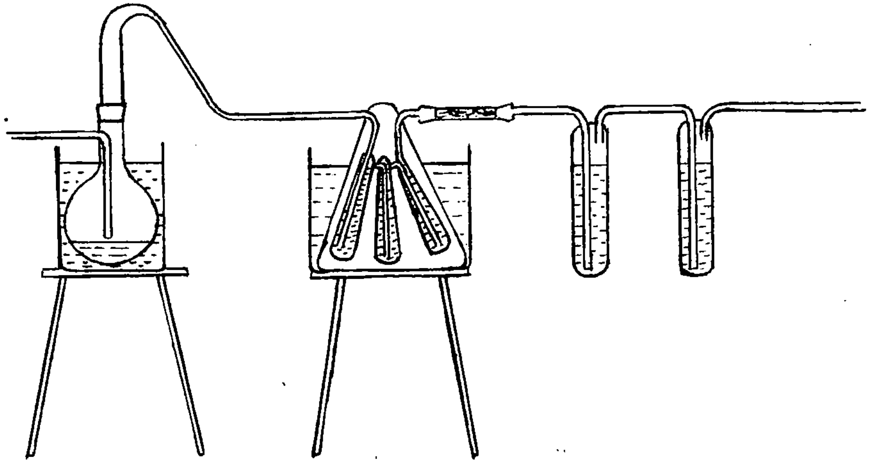
The free hydrogen chloride thus produced was blown into water and estimated by titration. The slight volatility of αnaphthoxy dichlorophosphine is sufficient to produce a blank, and a similar method suggested by Van Nieuwenberg[160] using cinnamoyl chloride is advantageous because of the lower volatility of the latter compound.

Cinnamoyl chloride was prepared by reacting 37.5 gms cinnamic acid with 45 gms of thionyl chloride in a long-necked flask fitted with a side arm. The flask was stoppered and a calcium chloride tube fitted to the side arm. The temperature was then gradually increased to 60°C. and held at this level for two hours. Excess thionyl chloride was removed by distillation at 30 mms and then the cinnamoyl chloride fraction collected, B.P.$_{11\text{mm.}}$131°C. The product was purified by a further distillation and stored in vacuo. Cinnamoyl chloride reacts instantaneously with water with the evolution of hydrogen chloride:-

$$C_6H_5CH{=}CH\text{-}COCl + H_2O \longrightarrow C_6H_5CH{=}CH\text{-}COOH + HCl$$

The apparatus employed is shown in Figure XXIII. It consisted of a reaction flask A through which could be swept a slow

Figure XXIII.



stream of phosphorous pentoxide dried nitrogen at constant velocity. The flask was fitted with a small air condenser to ensure the condensation of high boiling decomposition products, but the water vapour produced during the decomposition did not condense and was swept through a triple bubbler maintained at 40°C. containing cinnamoyl chloride, and the hydrogen chloride thus produced passed into a bubbler train containing distilled water.

One gm. of tetralin hydroperoxide was weighed into the reaction flask and dissolved in 2.5 mls of sodium dried tetralin. A slow stream of dry nitrogen was then swept through the flask at a steady rate until a constant blank titration was obtained. The temperature of the reaction flask was then increased to 140°C. and the apparatus maintained under standard conditions until the decomposition of the peroxide was complete. The contents of the water bubblers were then titrated with $\frac{N}{10}$ sodium hydroxide and the calculated blank titration subtracted.

Dean and Stark Method.

Water estimation by the Dean and Stark method was carried out in the all glass apparatus shown in Figure XXIV, the receiver vessel of which was calibrated to 0.05 ml. In order to minimise errors it was necessary to use large quantities of tetralin hydroperoxide for each estimation since, even if a complete dehydration reaction was assumed, only

18 mls of water would be obtained from 164 gms of the hydroperoxide.

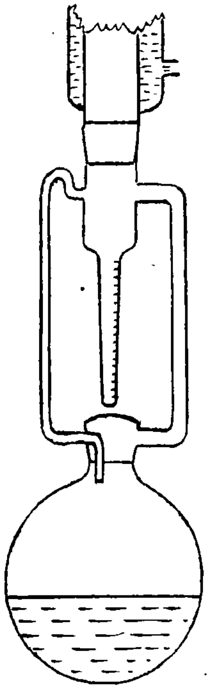


Figure XXIV.

16.4 gms. of tetralin hydroperoxide were weighed into the flask and dissolved in 75 mls of calcium chloride dried chlorbenzene. The flask was flushed with nitrogen and the temperature was gradually increased to 135°C. and held at this point until decomposition was complete. Dry toluene was then added and the temperature increased to distillation point. Attempts to increase the accuracy of the method by decreasing the diameter of the receiver tube were unsuccessful because of increased drop adhesion to the glass walls.

Estimation of Oxygen.

Estimation of oxygen was carried out by the standard method of absorption in alkaline pyrogallol solution. One gm.

of the hydroperoxide was weighed into the reaction flask (Figure XXV) and dissolved in 10 mls of chlorbenzene and the apparatus purged with nitrogen.

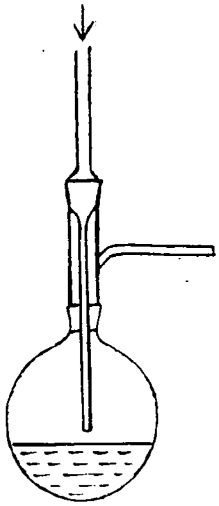


Figure XXV.

The exit tube was connected to a gas pipette and the temperature of the reaction flask increased to 140°C. When the decomposition of the hydroperoxide was complete the gaseous products were swept into the gas pipette in a stream of nitrogen and then analysed in the usual manner. A blank oxygen estimation on the nitrogen purge gas employed showed none to be present.

Experimental Method.

0.5 gm. of tetralin hydroperoxide was dissolved in 5 mls. of tetralin and decomposed by heating for 5 hours at 135°C. in an atmosphere of nitrogen to prevent solvent oxidation. This vigorous thermal treatment was necessary to destroy all the hydroperoxide present to prevent interference with analytical methods. In the case of the estimation of the alcohol, 1 gm. of the hydroperoxide was employed and the water produced during the decomposition was removed by azeotropic distillation with benzene prior to acetylation. In some cases, especially those involving long periods of refluxing, sufficient re-peroxidation occurred of the tetralin used as solvent to decolourise the indicators employed. This re-peroxidation was avoided by substitution of chlorobenzene as solvent and identical analytical results were obtained. Table XVI shows the results obtained.

Table XVI.

Analysis of Products of the Thermal Decomposition of Tetralin Hydroperoxide.

							Molar %
Ketone (as α Tetralone)	.499	gm.	≡	14.1	mls.	1.036 $\frac{N}{10}$ NaOH	48.0
Alcohol(" α Tetralol)	1	"	≡	9.1	"	$\frac{N}{5}$ NaOH	30.0
Acid (" mono-basic)	.503	"	≡	2.3	"	$\frac{N}{10}$ NaOH	7.5
Saponifiable material	.502	"	≡	1.5	"	$\frac{N}{10}$ NaOH	5.0
Water (Dean & Stark)	16.4	"	≡	1.0	"	H_2O	55.5
(Cinnamoyl chloride)	1	"	≡	33.2	"		54.5
Oxygen	1	"	≡	2.0	"		1.46

Tchoubar(161) has prepared 1:2-dihydronaphthalene oxide by the action of benzoyl peroxide on the hydrocarbon, and the possible formation of epoxides during the decomposition of tetralin hydroperoxide was investigated by (a) carrying out a prolonged hydroperoxide decomposition for 14 hours, and (b) dissolving the products of the normal thermal decomposition in acetone and hydrolysing with 25 mls. dilute hydrochloric acid. Results are shown in Table XVII. No appreciable variation in the alcohol-ketone ratio was observed, and it was assumed that epoxide formation did not take place. Even if momentary epoxide formation did take place, a rapid isomerisation to β tetralone would probably occur and oxidation of the latter would be immediate under the experimental conditions employed.

Table XVII.

Test for the Presence of Epoxides in the Products of Decomposition.

	Tetralol	Tetralone
Prolonged decomposition	-	49%
Hydrolysis of product with HCl	30%	47%
Normal thermal decomposition	30%	48%

Medvedev and Podyapolskaya(93) suggested that the decomposition of tetralin hydroperoxide involved the intermediate formation of a hydroxy peroxide resulting from reaction between α tetralone and the hydroperoxide, and showed experimentally that an equilibrium existed between α tetralone and the hydroperoxide. According to Medvedev and Podyapolskaya, a solution of the hydroperoxide in α tetralone reached an equilibrium after approximately seven hours, the hydroperoxide concentration still being constant after 80 hours reaction at 76°C. Repetition of this experiment under identical conditions gave contrary results. 3.0195 gms. of tetralin hydroperoxide were dissolved in 7.0235 gms. of α tetralone and heated in nitrogen at 76°C. Results shown in Table XVIII below give no evidence for the existence of an equilibrium.

Table XVIII.

The Decomposition of Tetralin Hydroperoxide in α Tetralone at 76°C.

Time after start of Decomposition (hrs)	Weight Sample (gms.)	Titration mls. $\frac{N}{10}$ $Na_2S_2O_3$	Hydroperoxide content per gm.
4	0.560	16.5	0.242
30	0.517	11.6	0.184
58	0.554	6.4	0.095
84	0.557	1.7	0.025

Milas(162) has shown that hydroxy peroxides of the type suggested by Medvedev and Podyapolskaya react very slowly, if at all, with potassium iodide and quantitative results were only obtained if the sample was refluxed with a mixture of sodium iodide, acetic acid and acetone. A sample of hydroperoxide in α tetralone was, therefore, partially decomposed and peroxide determination carried out using the standard and the Milas techniques, but as shown in Table XIX identical results were obtained and it appeared that there was little evidence for the formation of the hydroxy peroxide during the decomposition.

Table XIX.

Test for the Presence of a Hydroxy Peroxide.

	Total Peroxide Present Expressed as Tetralin Hydroperoxide/gm.
Normal Technique	.024
Milas "	.023

The variation of the velocity of the hydroperoxide decomposition with concentration suggested the possible variation of comparative yields of products with concentration, and a decomposition was therefore carried out in concentrated solution. The ketone value obtained, however, was not significantly different from that obtained in dilute solution (see Table XX).

Table XX.

Effect of Concentration on the Products of Decomposition

Concentration of Hydroperoxide	Tetralone
0.5 gm./5 mls	48.0%
1.0 " /5 "	49.5%

Only a very small evolution of oxygen was observed during the thermal decomposition in comparison with the amount produced during the low temperature metal catalysed decomposition (see Section IX) and this was probably related to utilisation of the oxygen produced for the further oxidation of the reaction mixture at the high temperature employed (140°C.).

Discussion.

The results obtained do not fit in with the conclusions of either Medvedev and Podyapolskaya(93) or George and Robertson(95). According to Medvedev and Podyapolskaya the decomposition took place via a hydroxy peroxide, and according to George and Robertson the reaction was a typical dehydration. Both parties assumed that α tetralone was the chief product. Larsen, Thorpe and Armfield(110) made a quantitative examination of the products of oxidation of aromatic naphthalenes at 110°C. Average results obtained for this type of compound are shown below:-

Acid	Saponification Total	Saponification Combined	Peroxide	Alcohol	Carbonyl
6.1	29.3	23.1	4.3	8.5	27.2

Water	CO_2	Volatile Acids
16.7	1.2	0.4

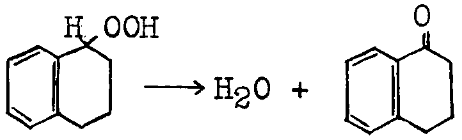
The relatively low alcohol value may be accounted for by ester formation, but all the analyses are of extremely doubtful validity because they were carried out in the presence of the hydroperoxide which, in the majority of cases, can react with the reagents used (e.g. hydroxylamine hydrochloride and sodium hydroxide).

The presence of α tetralol among the products of decomposition is confirmed by the work of Sully(60) and by the French Patent No.37,351 which covers the preparation of

∝tetralone and ∝tetralol by the autoxidation of the hydrocarbon.

The high temperature which had to be employed to achieve the complete decomposition of the hydroperoxide within a finite period, unfortunately also favoured the incidence of side reactions such as acid and ester formation, which tended to obscure the true ketone-alcohol ratio in the product. This difficulty may only be avoided if lower temperatures of decomposition are adopted and analysis of the products is made at partial conversion. This is not possible using the normal chemical analytical technique because of the interaction of undecomposed hydroperoxide with other reagents, but adoption of a polarographic technique may well overcome this difficulty. Stern and Polak(163) have already measured the reduction potentials of a number of organic peroxides, and a further application of the method would almost certainly provide a means of estimating alcohol and ketone concentrations at partial hydroperoxide conversions. This method would also enable a more accurate measure of the alcohol content to be made, for in the methods outlined above the value obtained for the ∝tetralol concentration is too high because the acetylation method adopted gives a measure of the total hydroxyl groups present in which will be included that of the o.phenol butyric acid, which is a minor product of the decomposition.

The relatively small percentage of α tetralone produced showed that the decomposition could not entirely be represented by the dehydration reaction



and the presence of hydroxylated compounds suggested that hydroxyl radicals were produced during the decomposition. The concentration and solvent effects which have already been discussed, and the fact that the hydroperoxide was a catalyst for the autoxidation, were strong evidence that free radicals were produced during the decomposition, and this theory was supported by the use of tetralin hydroperoxide as a catalyst for diminishing ignition delay in fuel injection engines(164). In view of the fact that George and Robertson had preferred an energy chain mechanism to a radical chain mechanism, it was felt desirable to obtain, if possible, further evidence of the presence of free radicals during the hydroperoxide decomposition and to attempt to identify the radicals concerned.

(c) Evidence of the Presence of Free Radicals during the Decomposition of Tetralin Hydroperoxide.

Polymerisation.

The polymerisation of olefines may be best explained either as a chain reaction involving free radicals or as a polar reaction involving a proton transfer. It has been shown that polymerisation processes involving radical chains may be catalysed by compounds which are themselves capable of undergoing decomposition with the production of free radicals. Thus, dibenzoyl peroxide which can undergo spontaneous decomposition to free phenyl and benzoate radicals is a very efficient catalyst for the polymerisation of liquid olefines such as styrene and methyl methacrylate. Similarly diazoacetates, which on decomposition produce free aryl radicals, are good catalysts for polymerisation processes(165). The catalysis of radical chain polymerisations may, therefore, be accepted as very strong evidence that the added catalyst is undergoing decomposition with the production of active free radicals, and it is of significance that Medvedev has used tetralin hydroperoxide as a catalyst for the polymerisation of 2-chlorobutadiene(166, 167). Because of the importance of such evidence, it was decided to investigate further the efficiency of tetralin hydroperoxide as a polymerisation catalyst. Experiments were, therefore, carried out with styrene, methyl methacrylate and acrylonitrile using tetralin hydroperoxide as catalyst. Parallel experiments for comparative purposes were made using benzoyl peroxide as a catalyst and the pure compound without a catalyst. Table XXI shows the results obtained. It can be seen that tetralin hydroperoxide is a polymerisation catalyst of the same efficacy as benzoyl peroxide, and it may, therefore, be assumed that free radicals are produced during its decomposition.

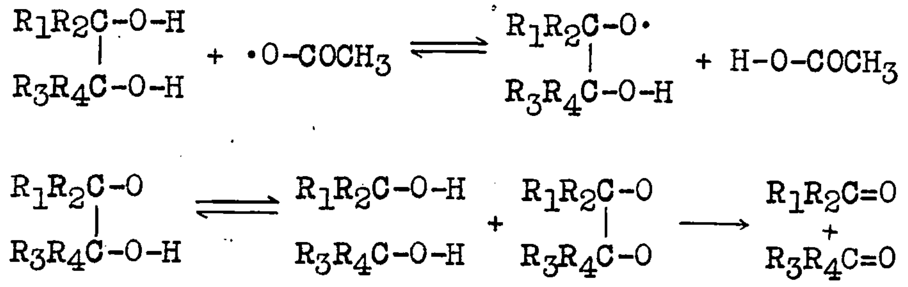
Table XXI.

Tetralin Hydroperoxide as a Catalyst for Polymerisation Processes.

Polymerisation	Peroxide	Conditions	Induction Period		Appearance
			Hrs	Mins	
Styrene (air atmosphere)	1% Tetralin Hydroperoxide	Heated at 115°C. in sealed tubes.	2	30	Solidified on cooling
	5% " "		2	0	- do -
	1% Dibenzoyl Peroxide		1	35	- do -
	5% " "		-	55	- do -
	None		> 3	0	Still mobile on cooling
Methyl Methacrylate (air atmosphere)	1% Tetralin Hydroperoxide	Heated at 50°C.	2	25	Viscous liquid
	5% " "		1	5	- do -
	1% Dibenzoyl Peroxide		-	30	- do -
	5% " "		-	25	- do -
	None		> 3	0	Mobile
Acrylonitrile (air atmosphere)	1% Tetralin Hydroperoxide	Heated at 55°C.	-	9	Polymer precipitated
	5% " "		-	5	- do -
	1% Dibenzoyl Peroxide		1	45	- do -
	5% " "		-	19	- do -
	None		> 2	0	Clear

Glycol Splitting.

Waters(136) has suggested that the splitting of ∝glycols to aldehydes and ketones by the use of lead tetra-acetate was due to dehydrogenation by free acetate radicals followed by a C-C bond fission:-



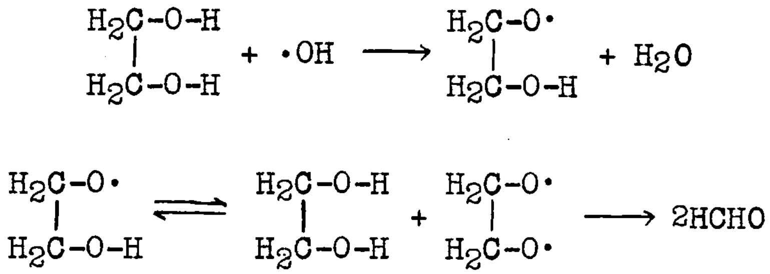
$$\begin{array}{c} R_1R_2C\text{-}O\text{-}H \\ | \\ R_3R_4C\text{-}O\text{-}H \end{array} + \cdot O\text{-}COCH_3 \rightleftharpoons \begin{array}{c} R_1R_2C\text{-}O\cdot \\ | \\ R_3R_4C\text{-}O\text{-}H \end{array} + H\text{-}O\text{-}COCH_3$$

$$\begin{array}{c} R_1R_2C\text{-}O \\ | \\ R_3R_4C\text{-}O\text{-}H \end{array} \rightleftharpoons \begin{array}{c} R_1R_2C\text{-}O\text{-}H \\ \\ R_3R_4C\text{-}O\text{-}H \end{array} + \begin{array}{c} R_1R_2C\text{-}O \\ | \\ R_3R_4C\text{-}O \end{array} \longrightarrow \begin{array}{c} R_1R_2C{=}O \\ + \\ R_3R_4C{=}O \end{array}$$

In support of such a theory Waters(168) has shown that the free hydroxyl radical is capable of effecting a similar splitting of glycols. Fenton's reagent (hydrogen peroxide plus a ferrous salt), which has been shown to produce free hydroxyl radicals (Haber and Weiss(88), Baxendale, Evans and Park(169)), reacts in solutions buffered with sodium acetate and acetic acid with both ethylene glycol and glycerol to produce some formaldehyde. Reaction with 2:3-butylene glycol gave both acetaldehyde and diacetyl. If tetralin hydroperoxide decomposed with the production of free hydroxyl radicals, it followed that it also should be capable of promoting ∝glycol splitting. A series of thermal decompositions of the hydroperoxide in various glycols as solvents were therefore investigated. The apparatus used was similar to that in Figure XXV consisting simply of a side arm flask and a nitrogen inlet. The gaseous products of the decomposition of the hydroperoxide were blown by a nitrogen gas stream through an air condenser and thence through a bubbler containing a suitable reagent.

Ethylene Glycol.

Five gms. of pure tetralin hydroperoxide were decomposed at 135°C. in 20 mls. of ethylene glycol. The gaseous products of reaction were blown through a bubbler containing a dilute alcoholic solution of dimedone. After warming the solution on a water bath traces of α tetralol were removed by steam distillation, and after cooling and repeated recrystallisation from dilute alcohol a small yield of crystals, M.P. 188°C., was obtained. The product gave no melting point depression with an authentic sample of the dimedone of formaldehyde. This glycol splitting by tetralin hydroperoxide may be represented as a function of the hydroxyl radical by the following mechanism:-

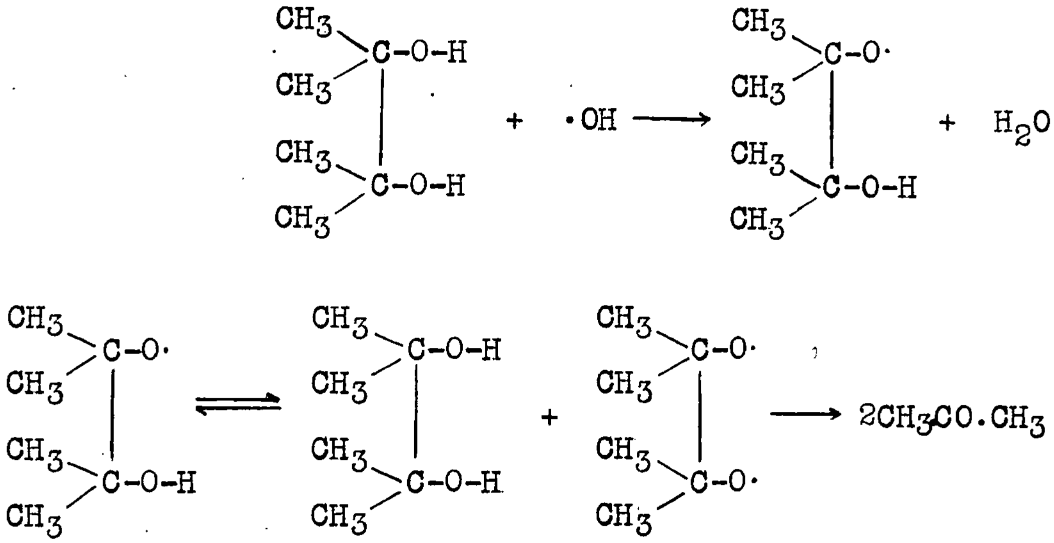


$$\begin{array}{c}H_2C{-}O{-}H\\|\\H_2C{-}O{-}H\end{array} + \cdot OH \longrightarrow \begin{array}{c}H_2C{-}O\cdot\\|\\H_2C{-}O{-}H\end{array} + H_2O$$

$$\begin{array}{c}H_2C{-}O\cdot\\|\\H_2C{-}O{-}H\end{array} \rightleftharpoons \begin{array}{c}H_2C{-}O{-}H\\|\\H_2C{-}O{-}H\end{array} + \begin{array}{c}H_2C{-}O\cdot\\|\\H_2C{-}O\cdot\end{array} \longrightarrow 2HCHO$$

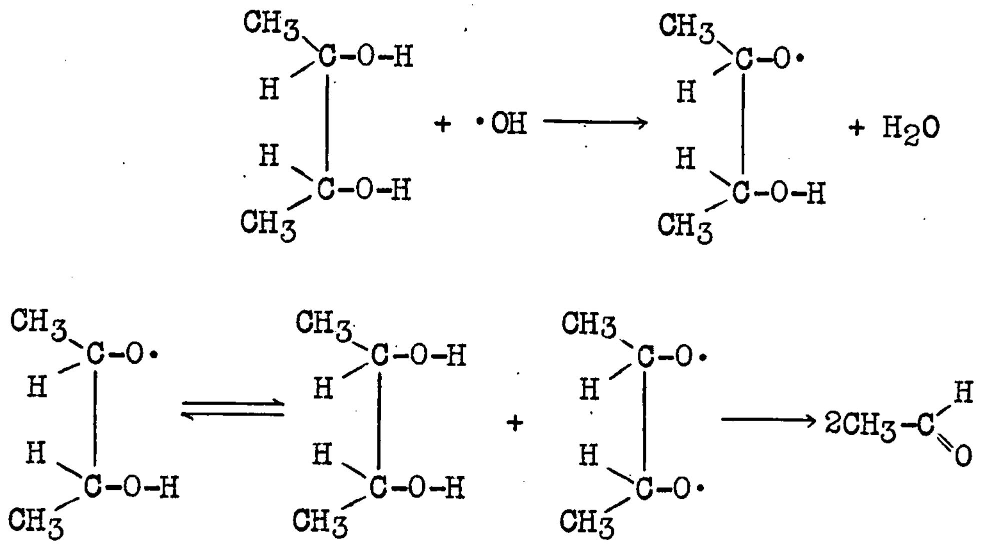
Pinacol.

Five gms. of tetralin hydroperoxide and 2 gms. of pinacol were dissolved in 20 mls. glacial acetic acid and the gaseous products of the decomposition at 135°C. blown through a solution of 2:4-dinitrophenyl hydrazine in dilute hydrochloric acid. A dinitrophenyl hydrazone was produced which, after recrystallisation from dilute alcohol, melted at 126°C. and, with an authentic sample of the dinitrophenyl hydrazone of acetone, gave a mixed melting point of 126°C. Aqueous solutions of the gaseous products of the decomposition gave confirmatory tests for acetone, producing a red colouration with an alkaline solution of sodium nitroprusside. The mechanism of this reaction may be represented as:-



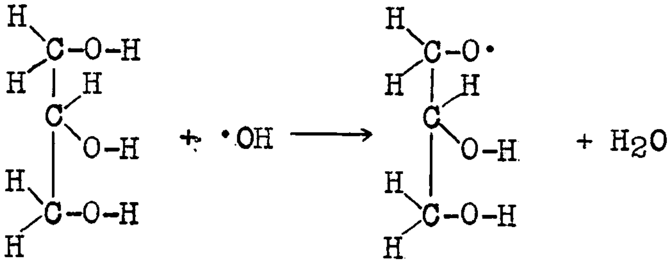
2:3-Butylene Glycol.

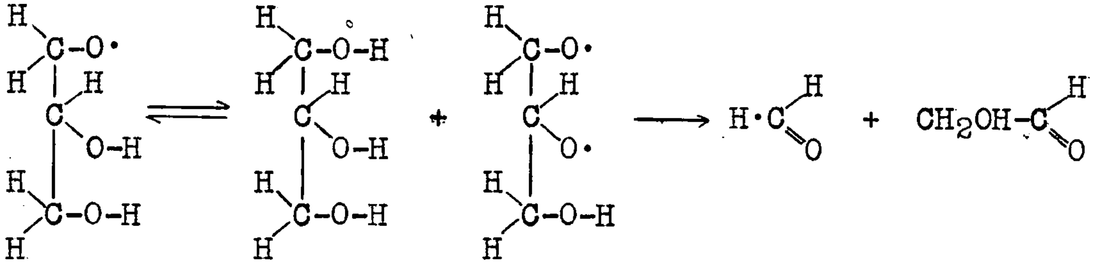
Five gms. of tetralin hydroperoxide were dissolved in 20 mls. of 2:3-butylene glycol and the gaseous products of the decomposition at 135°C. blown into a solution of dimedone in dilute alcohol. After digestion with acetic acid a dimedone anhydride derivative was produced which, after recrystallisation from dilute alcohol, melted at 175°C., and with an authentic sample of the dimedone anhydride derivative of acetaldehyde gave a melting point of 175°C. Aqueous solutions of the gaseous products of the decomposition gave confirmatory tests for acetaldehyde, addition of sodium nitroprusside and a drop of piperidine giving a deep blue colouration. The mechanism of the reaction may be represented as:-



Glycerol.

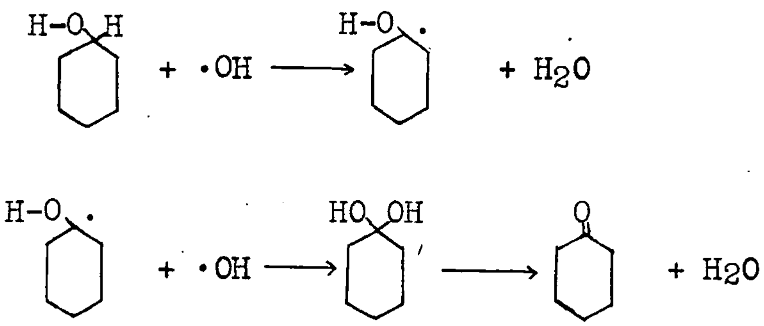
Five gms. of tetralin hydroperoxide were dissolved in 20 mls. of glycerol and the gaseous products of the decomposition blown into a solution of 2:4-dinitrophenyl hydrazine. A dinitrophenyl hydrazone was produced which, after recrystallisation from dilute alcohol, melted at 165°C., and with an authentic sample of the dinitrophenyl hydrazone of formaldehyde, gave a mixed melting point of 165°C. Aqueous solutions of the gaseous product gave confirmatory tests for formaldehyde forming a red ring with resorcinol and sulphuric acid. The mechanism of the reaction may be represented as:-





Cyclohexanol.

Any traces of cyclohexanone in a sample of cyclohexanol were removed by distillation of the latter from a little dinitrophenyl hydrazine. Two gms. of tetralin hydroperoxide were dissolved in 15 mls. of the purified cyclohexanol and decomposition carried out at 135°C. in an atmosphere of nitrogen. The product was distilled and the fraction, boiling at 155-160°C., collected. On shaking this fraction with a solution of dinitrophenyl hydrazine in dilute hydrochloric acid a dinitrophenyl hydrazone was produced which, after recrystallisation from dilute alcohol, melted at 162°C., and with an authentic sample of the dinitrophenyl hydrazone of cyclohexanone gave a mixed melting point of 162°C. The mechanism of this reaction may be represented as a breaking of the C-H bond, followed by hydroxylation and then loss of water.



Attack by hydroxyl radicals on alcohols to produce ketones has been confirmed by G.M. Henderson and P.V. Youll (private communication) who have shown that cyclohexanone was produced by the action of Fenton's reagent on cyclohexanol. Many workers have shown that attempts to oxidise alcohols in the liquid phase with gaseous oxygen produced only very small quantities of ketone, and it was therefore assumed that alcohols did not play an important role as an intermediate product. The above results, however, indicate that alcohols may be initially produced in higher yields than is apparent from ultimate analyses and hydroxyl radical attack on alcohols can thus function as a minor chain termination reaction in autoxidation processes.

Hydroxylation of Solvents.

The energy evolved in the reaction:-

$$\cdot OH + H \longrightarrow H_2O$$

has been shown by Dwyer and Oldenburg(170) to be 118 K.cals. per mol. The energy required to dissociate the C-H bond is of the order of 100 K.cals. and thus, from a consideration of the energy requirements, it is quite possible for the hydroxyl radical to attack the C-H bond. Evidence is available that such attack does occur. Cross et al showed that hydrogen peroxide in the presence of ferrous sulphate attacked furfural to produce hydroxy furfural(171), and benzene to produce phenol and catechol(172), and the latter observation was later confirmed by Oyamada(173). Martinon(174) also obtained catechol by the action of the same reagents on phenol, and Dakin et al(175) showed that even saturated hydrocarbons were slowly oxidised by warm solutions of hydrogen peroxide. Milas(176) has made an extensive investigation of hydroxylation using hydrogen peroxide and tertiary butyl hydroperoxide as a source of hydroxyl radicals, and vanadium pentoxide, osmic acid and chromium trioxide as metal catalysts. Cis glycols were formed from a number of unsaturated substances, and phenol and cresols were obtained from benzene and toluene respectively though at very small conversions (approximately 7%) and relatively poor yields (10-30%).

Attempts to obtain further evidence for the presence of the hydroxyl radical by decomposing tetralin hydroperoxide in suitable solvents and then examining the product for hydroxylated compounds were greatly hindered by the complex nature of the hydroperoxide decomposition and the fact that quantities of phenolic compounds, which were normally produced, tended to mask the presence of other hydroxylated products.

Decomposition of Tetralin Hydroperoxide in Benzene.

5 gms. of tetralin hydroperoxide were dissolved in 15 mls. of benzene and decomposed by the addition of cobalt naphthenate catalyst. Volatile products were removed by steam distillation and were then washed with sodium hydroxide. Phenolic substances were ether extracted after saturating the alkaline solution with sodium chloride and carbon dioxide. Removal of the ether left a yellow oil which absorbed appreciable quantities of bromine. The product of bromination was an oil which could not be crystallised even after storing at 0°C. The original steam distillate gave a blue colouration with ferric chloride, but since o.phenol butyric acid gave a similar colouration, such evidence was not of significance.

Decomposition of Tetralin Hydroperoxide in Chlorbenzene.

A solution of 16 gms. of tetralin hydroperoxide in 25 mls. of chlorbenzene was decomposed at 135°C. A small quantity of hydrochloric acid was detected among the decomposition products and gave confirmatory tests with silver nitrate. An alkali soluble brown tar was obtained, but further purification did not prove possible.

Decomposition of Tetralin Hydroperoxide in Chlornaphthalene.

Decomposition of 16 gms. of tetralin hydroperoxide in 25 mls. α chlornaphthalene gave similar results to that of chlorbenzene. Evidence of hydrogen chloride was obtained, but no definite phenolic product could be isolated.

Decomposition of Tetralin Hydroperoxide in p.Nitrotoluene.

A solution of 16 gms. of tetralin hydroperoxide in 30 mls. of pure benzene was decomposed at 90°C. in the presence of 14 gms. of p.nitrotoluene by the addition of cobalt naphthenate catalyst. The benzene was removed by distillation and the tarry residue extracted with hot distilled water in which p.nitrobenzyl alcohol is appreciably soluble. The aqueous extract, however, gave only a small yield of a high melting product, and it was assumed that no p.nitrobenzyl alcohol had been formed during the decomposition.

Decomposition of Tetralin Hydroperoxide in Nitrobenzene.

A solution of 16 gms. of tetralin hydroperoxide in 25 mls. of nitrobenzene was decomposed at 135°C. The products of the decomposition were washed with sodium hydroxide and phenolic substances removed from the alkali layer by acidification with hydrochloric acid followed by ether extraction. After ether removal, a brown tar was obtained which was not steam distillable, indicating that o.nitrophenol was not present. The tar was dissolved in chloroform and treated with a solution of bromine in the same solvent. A yellowish brown precipitate was formed which, after recrystallisation from dilute alcohol, melted at 134-137°C. Further recrystallisation gave no improvement in melting point and no characteristic analysis could be obtained, although a low nitrogen content indicated that some attack on the nitro group had occurred.

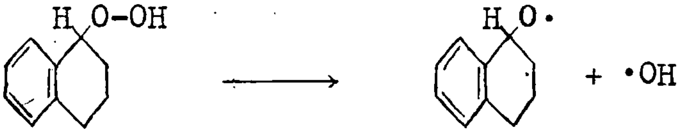
Decomposition of Tetralin Hydroperoxide in m.Dinitrobenzene.

A mixture of 16 gms. of tetralin hydroperoxide and 30 gms. of m.dinitrobenzene was gently heated until molten. The temperature was then gradually increased to 135°C. and held at this level for three hours. The products of the decomposition were washed with sodium hydroperoxide, and phenolic substances removed by acidification with hydrochloric acid followed by ether extraction. After ether removal the product was brominated and gave a yellowish brown precipitate. Recrystallisation from dilute alcohol gave a product melting at 208-210°C. The product gave no characteristic analysis after further purification, and it appeared probable that some attack on the nitro group had occurred.

Failure to obtain hydroxylation of nitro compounds with tetralin hydroperoxide is not entirely surprising in the light of Medvedev's work on polymerisation. Medvedev and Chilikina(167) showed that the presence of nitro compounds (e.g. dinitrobenzenes, p.nitroaniline) greatly increased the efficiency of tetralin hydroperoxide as a catalyst for the polymerisation of chloroprene. If, however, appreciable hydroxyl attack on the nitro compound took place, it would be expected that since the number of chain initiators available for the polymerisation process had decreased, the addition of nitro compounds should have a retarding effect. The attack of the hydroxyl radical on the C-H bond in aromatic systems appears to be a border line case for Milas(176), under very favourable conditions, only succeeded in obtaining very small overall yields (~6%), and the attack of the hydroxyl radical on an activated side chain (as in the case of tetralin) seems much more probable. Unfortunately, those compounds most suited to diagnostic testing of the presence of the hydroxyl radical are those which, being susceptible to hydroxyl radical attack, are themselves capable of undergoing autoxidation. Results from such experiments are, in consequence, of doubtful validity since any hydroxylated products obtained may have arisen from the normal oxidation chain. It may be concluded that intramolecular attack by the hydroxyl radical will invariably occur in the case of tetralin hydroperoxide unless compounds of a similar type (i.e. containing activated groupings especially susceptible to attack) are also present.

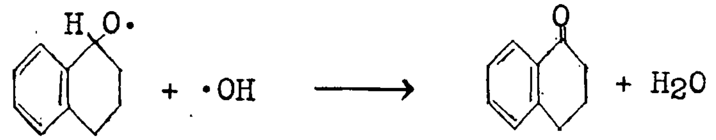
Discussion.

The experiments described in the previous part of this Section supply strong evidence that free radicals and, in particular, free hydroxyl radicals are produced during the decomposition of tetralin hydroperoxide. The decomposition was shown to be substantially unimolecular, and the primary bond fission may be represented by the following reaction:-

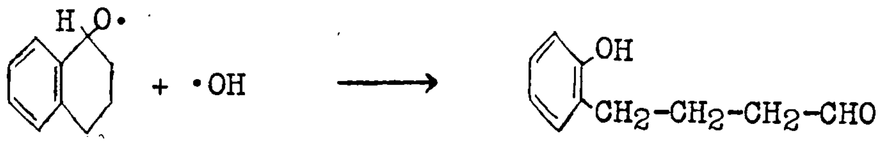


The quantity of hydroxyl radicals available for attack on vicinal molecules is limited by the following intramolecular processes which occur before the radicals can transfer from their immediate environment:-

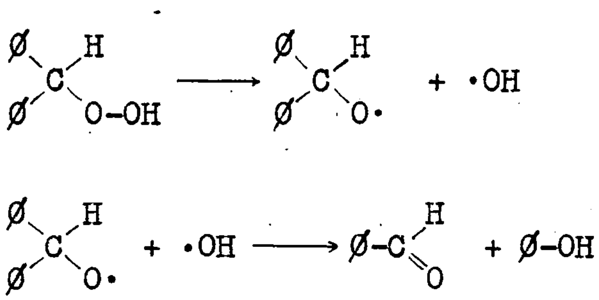
(1) Production of ∝ tetralone and water by the reaction:-



(2) Production of o.phenol butyraldehyde by fission of the C-C bond adjoining the aromatic ring, followed by hydroxyl radical attack on the aromatic ring:-



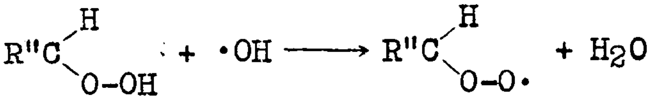
This fission of the C-C linkage adjacent to the aromatic ring also occurs during the thermal decomposition of tetralin as is evident from the formation of propenyl, butenyl and allyl benzene(177). Hydroperoxide decomposition of type (2), involving a fission of the O-O bond, followed by fission of the C-C bond of the carbon atom of the activating double bond, and attachment of the hydroxyl radical to the latter carbon atom, may be of general applicability. Hock and Lang(26), for example, have shown that diphenyl methyl hydroperoxide decomposes to produce phenol and benzaldehyde, and this may be represented as:-



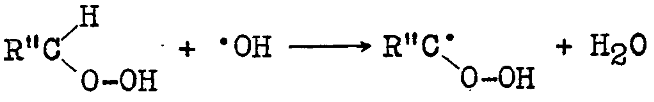
The energy necessary to bring about a C–C bond fission (81 K.cals.(146)) is more than offset by the energy released in the formation of a C=O bond (174 K.cal.(146)) from a C–O bond (87 K.cals.(145)).

The production of hydroxyl radicals during the decomposition of organic hydroperoxides as in the above reactions is supported by the fact that tertiary butyl hydroperoxide has been employed as a hydroxylating agent(176), and British Patent No.540,370 covers the use of organic hydroperoxides such as those produced during the oxidation of propane for the same purpose.

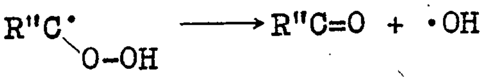
The intramolecular processes (1) and (2), as can be seen from the analytical results obtained, constitute the mode of decomposition of some 50% of the hydroperoxide and are accentuated by the cage effect of surrounding molecules. Franck and Rabinowitch(157) first applied the consideration of the cage effect to photolysis in solution, the essential idea being that two fragments from the dissociated molecule find themselves held in a cage of solvent molecules, and therefore the radical pair collide many times with each before they can diffuse apart. If the radicals can interact with a low activation energy, then appreciable reaction may occur before the two components can separate. The exact mode of the formation of the remaining 50% of the decomposition products is dependent upon radical-molecule and radical-radical interaction, and a selection of these reactions which constitute the chain starting and chain terminating processes of the main oxidation sequence must be made, not only in the light of qualitative and quantitative analytical results, but also in consideration of the observed kinetics of the oxidation obtained by George and Robertson(95). It could be assumed, for example, that after the primary bond fission to produce free hydroxyl radicals, these latter could attack the hydroperoxide molecule to produce either the hydroperoxide radical (reaction 3) or the ketone (reactions 4 and 5).



$$R''C\begin{array}{l}\diagup H\\ \diagdown O\text{-}OH\end{array} + \cdot OH \longrightarrow R''C\begin{array}{l}\diagup H\\ \diagdown O\text{-}O\cdot\end{array} + H_2O \qquad (3)$$

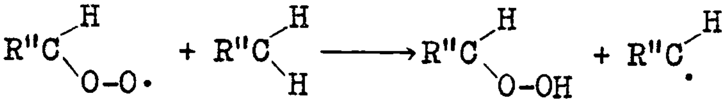


$$R''C\begin{array}{l}\diagup H\\ \diagdown O\text{-}OH\end{array} + \cdot OH \longrightarrow R''C^{\cdot}\diagdown O\text{-}OH + H_2O \qquad (4)$$



$$R''C^{\cdot}\diagdown O\text{-}OH \longrightarrow R''C{=}O + \cdot OH \qquad (5)$$

Reaction (3) would account for the catalysis of the autoxidation by tetralin hydroperoxide, for the hydroperoxide radical which is formed also takes part in the main oxygen uptake cycle described in Section IV.



$$R''C{\overset{H}{\diagup}\atop\underset{O-O\cdot}{\diagdown}} + R''C{\overset{H}{\diagup}\atop\underset{H}{\diagdown}} \longrightarrow R''C{\overset{H}{\diagup}\atop\underset{O-OH}{\diagdown}} + R''\overset{\diagup H}{\underset{\cdot}{C}}$$

The above mechanism is not applicable to the autoxidation of tetralin since it does not give rate expressions in agreement with observed results, and a detailed consideration of the chain starting and termination reactions involved in the autoxidation is given in Section VII.

VI. QUALITATIVE EXAMINATION OF THE OXIDATION PRODUCTS OF TETRALIN.

When hydrocarbons are subjected to prolonged oxidation, the product is invariably a complex mixture of compounds whose constitution gives no diagnostic guidance as to the mechanism of the oxidation since such compounds are often produced by secondary reactions. Although the final products of oxidation in such a multi-stage process cannot, without caution, be related directly to the mechanism of the main reaction, an indication may be given of some of the stages employed, and a knowledge of ultimate products is essential to explain kinetic results obtained in later stages of the oxidation. This is especially the case if products are of a phenolic nature and may, by their powers of inhibition, appreciably reduce the reaction rate. A sample of tetralin which had been oxidised under the conditions already described (see Section II) was carefully heated until all the hydroperoxide had decomposed. The peroxide-free solution was then distilled at reduced pressure and the following fractions were obtained:-

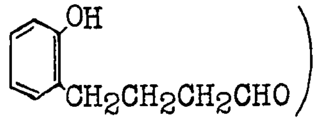
B.P.$_{15\text{ mm.}}$ 88°C.

This fraction consisted almost entirely of unchanged tetralin, but was found to give reactions indicative of the presence of 1:2-dihydronaphthalene. The fraction also rapidly absorbed bromine at 0°C. whereas pure tetralin reacted very slowly at this temperature. In order to obtain a quantitative estimate of the unsaturated compounds present, 20 mls. of the fraction were added to 70 mls. of an $\frac{N}{10}$ solution of bromine in carbon tetrachloride at 0°C. and stood in the dark for one hour. A blank sample containing 20 mls. of pure tetralin was treated in identical fashion, and after standing the excess bromine was, in both cases, titrated with $\frac{N}{10}$ sodium thiosulphate. 59.0 mls. of $\frac{N}{10}$ bromine solution were required and, expressed in terms of 1:2-dihydronaphthalene, 2% of unsaturated compounds were present. Attempts to obtain a crystalline sample of the dibromo derivative failed because of the excess of tetralin present.

B.P.$_{13\ mm.}$ 130°C.

The fraction was pale yellow in colour and of an oily consistency. It had the typical peppermint odour of αtetralone and gave an oxime by the standard method which, after recrystallisation from dilute alcohol, melted at 103°C., and, with an authentic sample of the oxime prepared from αtetralone, gave a mixed melting point of 103°C. αTetralol has the same boiling point as αtetralone, and, if a product of the oxidation, it would be present in the same fraction. A sample of the fraction was, therefore, refluxed with phenyl isocyanate for two hours and the product then steam distilled to remove the unchanged αtetralone. The mixture which remained as residue consisted of the phenyl urethane of tetralol (if present) and the substituted urea produced from the excess phenyl isocyanate. The residue was extracted with petroleum ether (60-80°C.) and the extract, after ether removal gave a product which, when recrystallised from alcohol, melted at 122°C., and with an authentic sample of the phenyl urethane of ∝tetralol gave a mixed melting point of 122°C. Separation of ∝tetralol from ∝tetralone can also be achieved by treating the mixture with finely ground calcium chloride. The ∝tetralone forms a solid calcium chloride complex whereas the ∝tetralol remains unchanged and can be collected as filtrate. ∝Tetralone can be recovered from the calcium chloride compound by treating the latter with water.

B.P.$_{.4 \text{ mm.}}$ 128°C.

The fraction was yellow in colour and of a viscous nature. Reaction with dinitrophenyl hydrazine gave a dinitrophenyl hydrazone which, after recrystallisation from dilute alcohol, melted at 149°C. and analysed C 56.0%, H 4.9%, N 16.0%. Samples of the fraction rapidly coloured Schiff's reagent and, on warming, reduced Fehling's solution. After vigorous shaking and long standing, the fraction gave a bisulphite compound. On standing, the fraction slowly oxidised to give an acid, melting point 68°C., which gave no melting point depression when mixed with a sample of pure o.phenol butyric acid. A sample of the fraction analysed C 73.2%, H 7.1%. Calculated values for o.phenol butyraldehyde (

) are C 73.1%, H 7.3%.

B.P.$_{.4\ mm.}$ 128-200°C.

All attempts to obtain further definite fractions failed, the distillation temperature gradually increased, and an arbitrary cut was made at 200°C. The sample was found to be acidic, and on treatment with sodium hydroxide the solution momentarily turned a bluish green prior to turning brown in colour. The alkali extract, after acidification and ether extraction, gave a dark brown oil from which it was found to be extremely difficult to obtain a crystalline product. This was finally achieved by extracting with carbon disulphide as a solvent. The product was soluble in water and gave an acid reaction with litmus. It reacted with sodium bicarbonate solution giving carbon dioxide evolution and showing the presence of the carboxyl group. An aqueous solution of the compound decolourised potassium permanganate, coloured ferric chloride bluish green, and when diazotised with sulphanilic acid gave a red dye. After repeated purification by extraction of the aqueous solution with charcoal and recrystallisation of the product, a sample of the pure acid was obtained which, after prolonged vacuum drying, melted at 68°C. The presence of both phenolic and carboxylic groupings suggested the possibility that the compound was o.phenol butyric acid, and a sample of the pure acid was prepared in the following manner by application of the general method of Schroeter(178).

Fifteen gms. of pure α tetralone were dissolved in 40 mls. of methyl alcohol and cooled to 0°C. Forty gms. of finely ground potassium persulphate in 40 gms. of concentrated sulphuric acid at 0°C. were added with vigorous mechanical stirring. When the reaction was complete, the excess acid was neutralised with sodium hydroxide and the bulk of the methyl alcohol removed by distillation. The brown oil which then formed was extracted with ether and then distilled at reduced pressure, B.P.$_{15\ \mathrm{mm.}}$ 180°C. This methyl ester of the acid was hydrolysed by refluxing with 10% sodium hydroxide solution for one hour. Acidification and ether extraction gave a light brown crystalline product. After charcoal extraction of the aqueous solution and further recrystallisation a colourless product was obtained which melted at 68°C. after prolonged vacuum drying. An aqueous solution of the acid gave the same qualitative tests as the acid obtained from the products of the tetralin oxidation and gave a mixed melting point of 68°C. with the latter. A sample of the acid from the tetralin oxidation analysed C 66.2%, H 6.9%, acid equivalent 180. Theoretical values calculated for o.phenol butyric acid are C 66.6%, H 6.7%, acid equivalent 180.

Schroeter has reported a tendency of o.phenol butyric acid to undergo loss of water with resultant lactone formation, and this probably accounted for the difficulty in obtaining satisfactory fractionation. The bulk fraction had a very characteristic ester-like odour which may have been due to ester formation between tetralol and the free o.phenol butyric acid, although no separate fraction could be isolated.

B.P.$_{.4\ mm.}$>200°C.

This high boiling fraction consisted of an extremely viscous dark brown liquid. Alkali extraction gave a small quantity of a carboxylic acid melting at 164°C. which analysed for hydrocinnamic o.carboxylic acid

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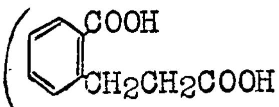


M.P. 164°C.)

Found C 62.5%, H 5.1%; Equivalent 100

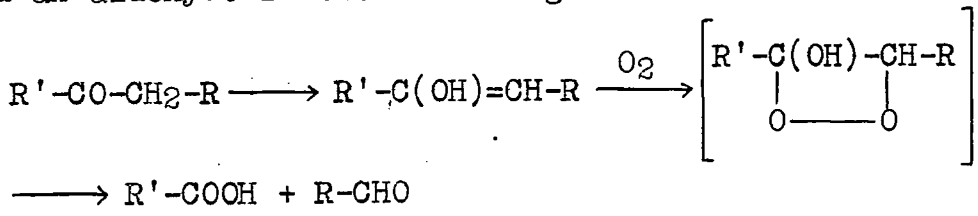
Calculated C 62.0%, H 5.1%; Equivalent 97

The acid, on fusing with sulphuric acid and resorcinol, gave a faint fluorescence as reported by Strauss and Lemmel(179).

Attempts were made to purify further the remaining tar which was almost insoluble in petroleum ether, but appreciably soluble in benzene. Chromatographic analysis of the benzene solution in ultra-violet light through an alumina column gave an impure fraction which fluoresced. The viscous pale yellow liquid thus obtained contained only a very small percentage of oxygen (C 89.0%, H 7.0%) and was thought to be an impure sample of the dimer of the tetralyl radical. Further purification, however, did not prove possible.

The Oxidation of Ketones.

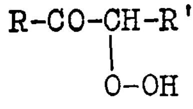
The presence of hydrocinnamic o.carboxylic acid among the products of tetralin oxidation was of interest because it provided evidence of the occurrence of a secondary ring fission process. It seemed probable that this type of ring fission might be related to a further oxidation of αtetralone, but little information was found to be available concerning the mechanism of the oxidation of ketones. Jenkins(180) drew attention to the fact that ketones of the type $R'\text{-}CO\text{-}CH_2\text{-}R$ could undergo autoxidation and gave strong peroxide reactions after exposure to air. He suggested that oxygen attacked the enolic form of the ketone to form a peroxide which then underwent decomposition to produce an acid and an aldehyde in the following manner:-



$$R'\text{-}CO\text{-}CH_2\text{-}R \longrightarrow R'\text{-}C(OH)\text{=}CH\text{-}R \xrightarrow{O_2} \left[\begin{array}{l} R'\text{-}\underset{\underset{O}{|}}{C}(OH)\text{-}\underset{\underset{O}{|}}{CH}\text{-}R \end{array}\right] \longrightarrow R'\text{-}COOH + R\text{-}CHO$$

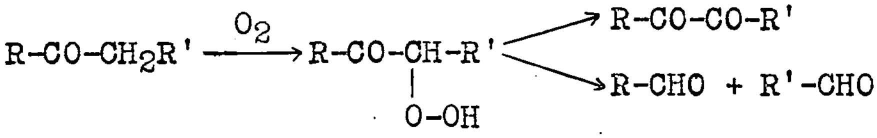
The liquid phase air oxidation of cyclic ketones to produce dicarboxylic acids has been the subject of a number of patents, but no indication has been given of the mechanism involved.

Paquot(181) investigated the oxidation of ketones in the presence of nickel phthalocyanine and obtained diketones, aldehydes and acids as products. He suggested that it was not necessary to postulate conversion to the enol form before reaction with oxygen, and preferred the theory that the >C=O group activated the adjacent methylenic group which then underwent oxidation to produce a peroxide of the type



$$R\text{-}CO\text{-}\underset{\underset{O\text{-}OH}{|}}{CH}\text{-}R'.$$

This peroxide could then decompose to a diketone or to aldehydes:-



$$R\text{-}CO\text{-}CH_2R' \xrightarrow{O_2} R\text{-}CO\text{-}\underset{\substack{|\\ O\text{-}OH}}{CH}\text{-}R' \begin{array}{l} \nearrow R\text{-}CO\text{-}CO\text{-}R' \\ \searrow R\text{-}CHO + R'\text{-}CHO \end{array}$$

The formation of a keto α hydroperoxide following the activation of the methylenic group adjacent to a >C=0 group fitted in well with the theories of Farmer and co-workers(47) on hydrocarbon oxidation, and it appeared highly probable that such a reaction would also be the first stage in the thermal oxidation of ketones. An investigation was therefore made of the thermal oxidation of cyclohexanone and α and β tetralone

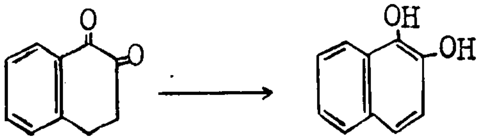
Cyclohexanone was purified by fractionation and oxidised at 75°C. by passing a brisk air stream through the solution. The rate of oxidation did not appear to be rapid and the temperature was increased to 100°C. After a short period the solution gave positive peroxide tests with potassium iodide and gave an acid reaction with litmus. After ten hours oxidation the solution was allowed to cool and a heavy crystalline precipitate was deposited. The crystals were removed by filtration and after recrystallisation from water gave a melting point of 151°C. On fusing a sample of the crystals with resorcinol and concentrated sulphuric acid and adding an excess of sodium hydroxide a crimson colouration was obtained and a mixed melting point of the crystals with a sample of authentic adipic acid gave no depression. Riley's(182) method for the isolation of diketones was employed. This involved reaction of the diketone in the enol form with potassium hydroxide.

The filtrate was washed three times with ice-cold 10% potassium hydroxide, and the alkaline extract shaken with ether to remove unchanged cyclohexanone. The excess alkali was neutralised with ice-cold hydrochloric acid, the solution saturated with sodium chloride, and then extracted with ether. The ether extract was dried with anhydrous sodium sulphate and the ether removed by distillation. The residual oil was vacuum distilled and the product, B.P.$_{20\ mm.}<100^{o}$C., collected. The distillation residue crystallised and consisted almost entirely of adipic acid. The fraction B.P.$_{20\ mm.}<100^{o}$C. darkened ferric chloride instantaneously, and a neutral solution of the oxime prepared in the normal way, when added to a neutral solution of nickel sulphate, gave a flocculent red precipitate of a nickel complex. Wallach(183), and Rauh and co-workers(184) have shown that the formation of a red nickel complex with neutral nickel salts is a characteristic of the dioxime of 1:2-cyclohexane dione. 1:2-Cyclohexane dione tends to decompose slightly to adipic acid even at 0°C. and it is not surprising that, under the vigorous oxidising conditions of the experiment, the greater part of the diketone underwent degradation. The ketone peroxide which was formed during the reaction was apparently of an unstable nature and attempts to isolate samples by the usual vacuum distillation technique were not successful.

β Tetralone resembles cyclohexanone in that it contains a methylenic group which is activated by an adjacent carbonyl grouping. In this case, however, the activation is much more marked because the methylenic group is also activated by its proximity to the benzene ring. A sample of β tetralone was exposed to atmospheric oxidation and after one week the solution had become viscous and crystal formation was observed. The crystals were separated from the viscous mother liquor by differential solubility in benzene. An aqueous solution of the crystals (which was strongly acidic) was extracted with charcoal, and a pure sample of the crystals thus obtained melted at 164°C. The product analysed for hydrocinnamic o.carboxylic acid (M.P. 164°C.).

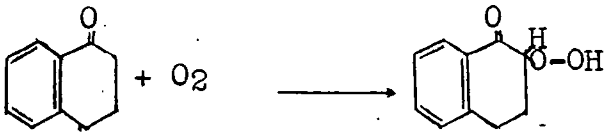
Found C 62.4%, H 5.1% Equivalent 100
Calculated C 62.0%, H 5.1% Equivalent 97

α Tetralone was oxidised at 100°C. by passing a brisk air stream through the solution which gradually turned yellow and finally orange-red in a way that strongly resembled the oxidation of tetralin. The solution gave a positive peroxide test and gave an acidic reaction with litmus. After 15 hours the solution was cooled to 0°C. and extracted with ice-cold sodium hydroxide. The alkaline extract was acidified, saturated with sodium chloride, and ether extracted. After the removal of ether an oxime of the residual oil was prepared in the usual way. Addition of nickel sulphate to a neutral solution of the oxime gave a reddish brown precipitate. The precipitate, which was slightly soluble in chloroform to give a pink solution, contained approximately 9% of nickel. More accurate analysis was not possible because the compound exploded on heating. A diketone of this type would be expected to be extremely unstable, and Strauss, Bernoully and Mautner(185) have suggested that in alkaline solution 1:2-tetralin dione tends to isomerise to the enolic form, β naphthohydroquinone

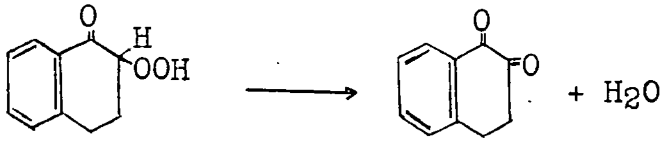


which then undergoes further oxidation with a series of colour changes through brown, green and orange. Colour reactions of α tetralone with sodium hydroxide are definitely related to the degree of oxidation - freshly prepared α tetralone gives a very weak colouration, and oxidised α tetralone gives progressively stronger reactions.

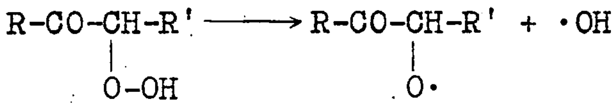
It may be concluded that there is strong evidence that the thermal oxidation of ketones takes place via the formation of an α hydroperoxide, e.g.



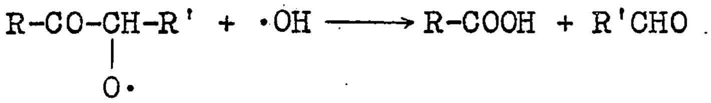
This hydroperoxide may then undergo dehydration to produce a diketone:-



or decompose with radical formation in a similar fashion to that described in Section V for hydrocarbon hydroperoxides. Non-cyclic ketones would undergo this radical decomposition with the formation of an aldehyde and an acid:-

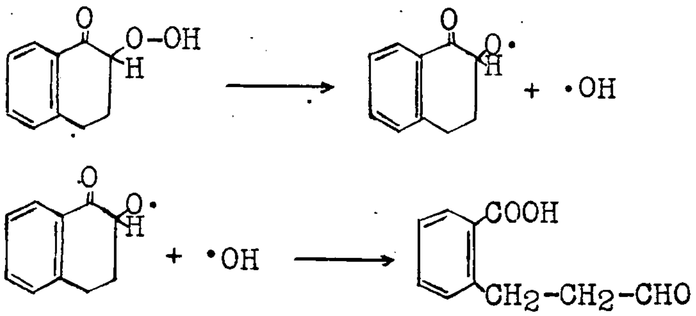


$$\text{R-CO-}\underset{\underset{\text{O-OH}}{|}}{\text{CH}}\text{-R}' \longrightarrow \text{R-CO-}\underset{\underset{\text{O}\cdot}{|}}{\text{CH}}\text{-R}' + \cdot\text{OH}$$



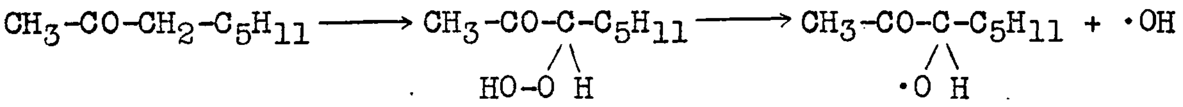
$$\text{R-CO-}\underset{\underset{\text{O}\cdot}{|}}{\text{CH}}\text{-R}' + \cdot\text{OH} \longrightarrow \text{R-COOH} + \text{R}'\text{CHO}$$

Cyclic ketones would undergo ring fission with aldehyde formation:-

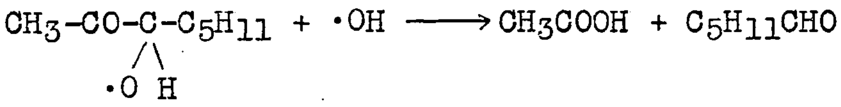


Under the strong oxidising conditions prevailing, aldehydic products would appear predominantly as the corresponding acids.

The results obtained by Paquot fit in well with the mechanism outlined above and indicate that C-C fission generally occurs between the carbon atom possessing the peroxide grouping and the adjacent carbon atom of the activating grouping. Thus Paquot obtained acetic acid, caproaldehyde and caproic acid from the oxidation of methyl hexyl ketone:-

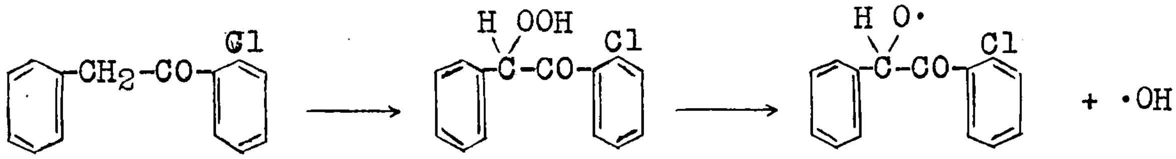


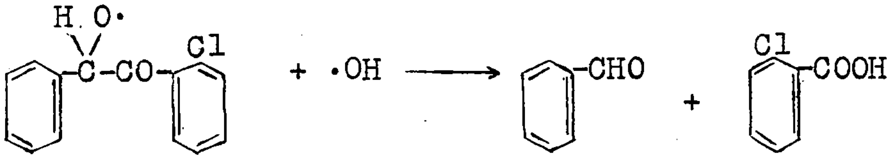
$$CH_3\text{-}CO\text{-}CH_2\text{-}C_5H_{11} \longrightarrow CH_3\text{-}CO\text{-}\underset{\substack{/\backslash \\ HO\text{-}O\ \ H}}{C}\text{-}C_5H_{11} \longrightarrow CH_3\text{-}CO\text{-}\underset{\substack{/\backslash \\ \cdot O\ \ H}}{C}\text{-}C_5H_{11} + \cdot OH$$



$$CH_3\text{-}CO\text{-}\underset{\substack{/\backslash \\ \cdot O\ \ H}}{C}\text{-}C_5H_{11} + \cdot OH \longrightarrow CH_3COOH + C_5H_{11}CHO$$

The formation of benzaldehyde and 2-chlorobenzoic acid during the autoxidation of benzyl 2-chlorophenyl ketone(180) may be similarly explained:-



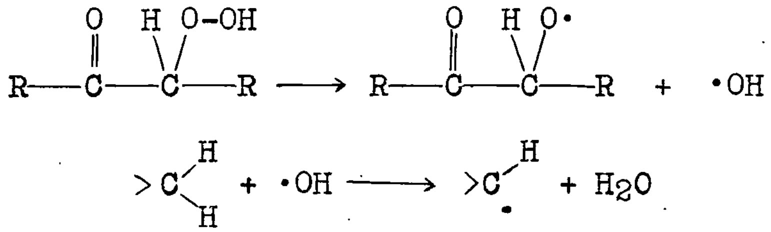


It is of interest to relate the above theory of ketone oxidation to the effect of ketones on the oxidation of hydrocarbons. Some workers have reported that ketones can be employed as initiators of hydrocarbon oxidations, but others have shown that ketones can exert an inhibitor action. The effect that ketone addition promotes is dependent upon:-

(1) The ease of oxidation of the added ketone relative to the hydrocarbon.

(2) The ease with which oxidation products of the added ketone can either rearrange or decompose to substances containing the hydroxyl grouping, which can then function as inhibitors.

If the ketone can undergo oxidation more easily than the hydrocarbon, then in the primary stages of the reaction a keto-hydroperoxide will be formed in preference to a hydrocarbon hydroperoxide. The keto-hydroperoxide may then undergo decomposition with the production of free radicals which can catalyse the oxidation of the hydrocarbon by production of a hydrocarbon radical which then reacts with oxygen (as described in Section IV). Thus:-

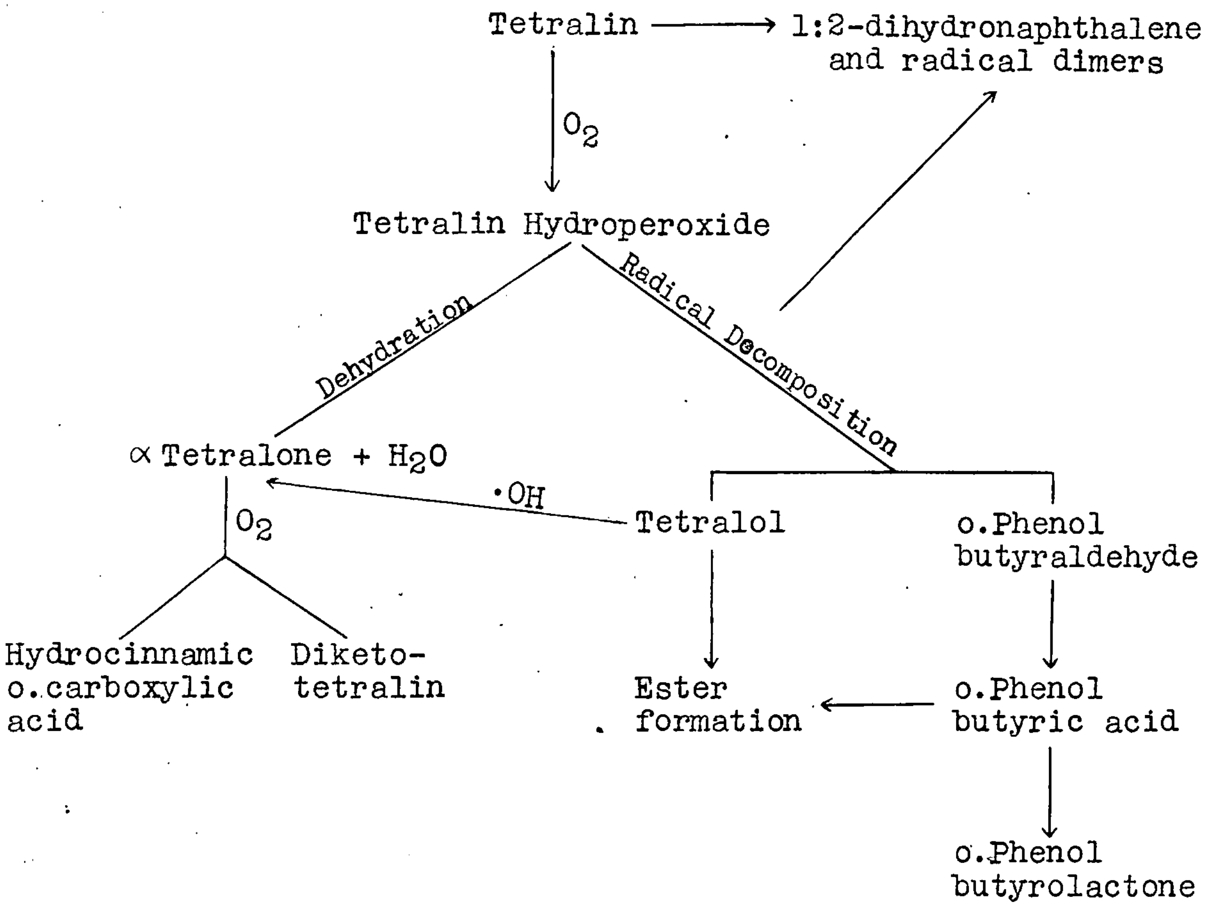


$$R-\overset{\overset{O}{\|}}{C}-\overset{H\ \ O-OH}{\overset{\diagdown\ \diagup}{C}}-R \longrightarrow R-\overset{\overset{O}{\|}}{C}-\overset{H\ \ O\cdot}{\overset{\diagdown\ \diagup}{C}}-R + \cdot OH$$

$$>C\begin{smallmatrix}\diagup H\\ \diagdown H\end{smallmatrix} + \cdot OH \longrightarrow >\underset{\bullet}{C}\diagup H + H_2O$$

If, on the other hand, the ketone undergoes oxidation more slowly than the hydrocarbon but does so with the production of substances which can easily rearrange to produce inhibitors, then ketone addition will exert a slight inhibitor effect. George and Robertson(95) have, for example, reported that ∝ tetralone is a mild inhibitor of tetralin oxidation.

Adopting the mechanism suggested for ketone oxidation and hydroperoxide decomposition, the following chart represents the possible products of thermal oxidation of tetralin:-


Tetralin
1:2-dihydronaphthalene and radical dimers
O_2
Tetralin Hydroperoxide
Dehydration
Radical Decomposition
∝ Tetralone + H_2O
•OH
O_2
Tetralol
o.Phenol butyraldehyde
Hydrocinnamic o.carboxylic acid
Diketo-tetralin
Ester formation
o.Phenol butyric acid
o.Phenol butyrolactone

The Effect of the Products of Decomposition on the rate of Oxidation.

It was shown in Section III that the rate of oxidation of tetralin gradually decreased as the reaction proceeded, and it was suggested that the products of the reaction probably contributed to this rate decrease. George and Robertson have shown that ∝ tetralone is a mild inhibitor of the oxidation in the preliminary stages, but it seemed much more probable that the o.phenol butyric acid produced during the reaction would exert a more marked inhibitor effect. One gm. of o.phenol butyric acid, prepared in the manner already described, was added to 25 mls. of a partially oxidised sample of tetralin and the rate of oxygen uptake at 76°C. compared with that of a sample of the tetralin without acid addition. Results given in Table XXII show that o.phenol butyric acid was a strong inhibitor of the oxidation of tetralin, and a gradual accumulation of the acid in the reaction mixture would account for a partial decrease in the rate of the oxidation.

Table XXII.

The Effect of o.Phenol Butyric Acid on the Oxidation of Tetralin

	Oxygen Uptake mls./15 minutes						
	Time after Start of Oxidation						
	15 mins	30 mins	45 mins	60 mins	75 mins	90 mins	105 mins
Partially oxidised tetralin.	4.3	4.6	4.9	5.4	5.7	-	-
Partially oxidised tetralin + 1 gm. o.phenol butyric acid.	2.2	1.9	1.7	1.4	1.0	0.9	0.5

VII. INTERPRETATION OF THE KINETICS OF THE THERMAL OXIDATION OF TETRALIN.

If (T) and (O_2) represent the tetralin and oxygen concentrations respectively, George and Robertson(95) found the following kinetic characteristics of the thermal oxidation:-

Uninhibited reaction	$R_o \sim (T)^2(O_2)^0$
Inhibited "	$R_i \sim (T)^2(O_2)^0$
Rate of chain initiation	$a \sim (T)(O_2)^0$
Induction period	$t_i \sim (RH)^{-1}(O_2)^0$

Assuming that for a stationary chain reaction:-

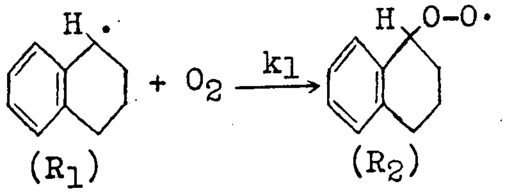
$$\text{Rate} = \frac{\text{chain initiation rate x propagation rate}}{\text{termination rate}}$$

then the chain propagation rate $\sim (T)(O_2)^0$ and the chain termination rate will be independent of T.

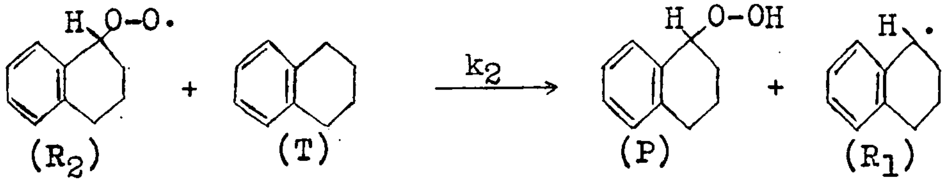
The kinetic relationship for the rate of reaction shown above corresponds, as has been shown in Section III, to the steady state reaction.

The Main Chain Reaction.

Strong evidence was given in Section IV that the main oxidation reaction could be represented by the following chain mechanism:-



(1)



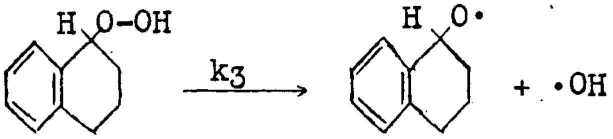
(2)

and the rate of reaction by the expression:-

$$\frac{-dO_2}{dt} = \frac{+dP}{dt} = k_1R_1O_2 = k_2R_2T \qquad (A)$$

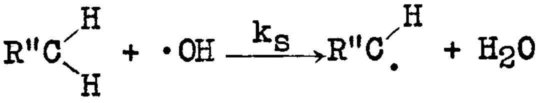
The Chain Initiation Process.

In Section V it was shown that the primary fission occurring during the decomposition of the hydroperoxide was that of the O-O bond:-



(3)

and that the hydroxyl radical could attack the C-H bond. It may be assumed, therefore, that under the normal conditions of thermal oxidation, the reaction



$$R''CH_2 + \cdot OH \xrightarrow{k_s} R''\dot{C}H + H_2O \qquad (4)$$

(T) (R_1)

can occur. The probability that this reaction occurs in the case of tetralin is very high since the less active acetate radical produced during the decomposition of lead tetra-acetate was found to be an active catalyst for the autoxidation (Section IV).

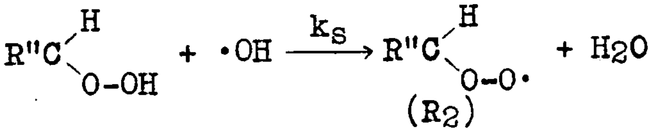
Reaction (4) is slightly exothermic (approximately 6 K.cals.) and the activation energy of the chain starting process obtained by George and Robertson (26 K.cals.) seems a reasonable value for this reaction. Initiation by reaction (4) would be especially favoured during the early stages of the reaction since the hydrocarbon concentration would be at a maximum and the corresponding probability of radical-radical interaction at a minimum. Reaction (4) gives as the rate of chain initiation the expression:-

$$\text{Rate} = k_s(OH)(T) \tag{B}$$

which, in accordance with the findings of George and Robertson, is of the first order with respect to the hydrocarbon and of zero order with respect to oxygen. The production of hydroxyl radicals during the decomposition of the hydroperoxide and the function of hydroxyl radicals as chain initiators explains the catalysis of the autoxidation of the hydrocarbon by the addition of the hydroperoxide.

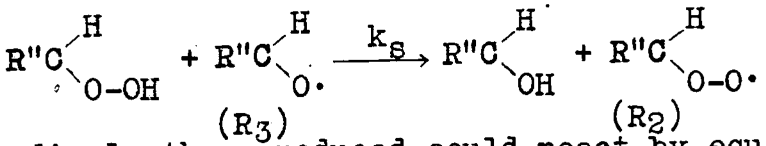
Alternative chain initiation could take place by:-

(1) Attack on the hydroperoxide by the hydroxyl radical



(5)

(2) Attack on the hydroperoxide by the alcohol radical



(6)

The peroxide radicals thus produced could react by equation (2) to produce the hydrocarbon radical which could then restart the main cycle. Such initiation processes would lead to the rate expressions:-

Rate of chain initiation = $k_s(OH)(P)$ for reaction (5), and
" " " " = $k_s(P)(R_3)$ " " (6)

which are not in accordance with the results obtained by George and Robertson.

Chain Termination Processes.

Radical interaction or dimerisation generally constitute the chain termination processes involved in oxidation reactions, and the following may be considered.

Dimerisation of R_1

This reaction would produce ditetralyl and, although not isolated as a pure product, indications were obtained of the occurrence in the oxidation products of a high boiling hydrocarbon fraction which fluoresced in ultra-violet light (Section VI). The analagous dimer of the phenyl ethyl radical, 2:3-diphenyl butane, was isolated by Sully(60) from the products of the oxidation of ethyl benzene. Small scale disproportionation of the tetralyl radical appeared to occur since evidence was obtained of the presence of 1:2-dihydronaphthalene.

Dimerisation of R_2 and Interaction of R_1 and R_2

Both reaction

$$ROO\cdot + ROO\cdot \longrightarrow R\text{-}O\text{-}O\text{-}O\text{-}O\text{-}R$$

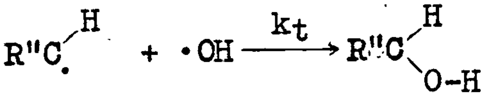
and

$$RCH\cdot + ROO\cdot \longrightarrow RCH\text{-}O\text{-}O\text{-}R$$

yield products which, resembling triphenyl methyl peroxide, may themselves undergo decomposition to produce radicals which function as autoxidation catalysts and cannot, therefore, be considered as main chain stopping processes.

George and Robertson demonstrated that if it was assumed that mutual free radical chain termination reactions of the above types occurred, then expressions were derived for the oxidation rate which did not agree with the observed rate dependency of the thermal oxidation, and on this basis rejected all radical chain mechanisms for the reaction. The three mutual chain termination reactions described above, however, are not the only possible termination reactions, and other possible alternatives are:-

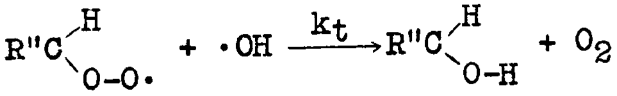
Interaction of the hydroxyl and hydrocarbon radicals:



$$R''\underset{\bullet}{C}{}^{\diagup H} + \cdot OH \xrightarrow{k_t} R''C\begin{smallmatrix}\diagup H\\ \diagdown O-H\end{smallmatrix} \qquad (7)$$

(R_1)

Interaction of the hydroxyl and peroxide radicals:



$$R''C\begin{smallmatrix}\diagup H\\ \diagdown O-O\cdot\end{smallmatrix} + \cdot OH \xrightarrow{k_t} R''C\begin{smallmatrix}\diagup H\\ \diagdown O-H\end{smallmatrix} + O_2 \qquad (8)$$

(R_2)

Both these termination reactions involve the hydroxyl radical, which is also the chain initiator, and result in the formation of α tetralol.

Other chain termination reactions include surface reactions, and reactions with inhibitors and reaction products such as o.phenol butyric acid and tetralol, and these may be represented:-

$$R_1 + I \longrightarrow \text{Inert products} \qquad (9)$$

$$R_2 + I \longrightarrow \text{Inert products} \qquad (10)$$

Reactions (7) and (8) satisfy the condition that the same catalyst is involved in both the chain starting and termination processes which, as shown by George, Rideal and Robertson(13), is an essential feature of autoxidations which proceed at a steady rate.

Chain Termination by Reaction (7).

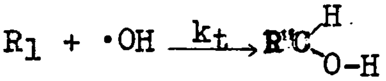
Assuming the chain cycle:-

Chain initiation $T + \cdot OH \xrightarrow{k_s} R_1 + H_2O$ (3)

Main chain $R_1 + O_2 \xrightarrow{k_1} R_2$ (1)

$R_2 + T \xrightarrow{k_2} P + R_1$ (2)

Chain termination



$R_1 + \cdot OH \xrightarrow{k_t} R'C\begin{smallmatrix}H\\ O-H\end{smallmatrix}$ (7)

then in the steady state:-

$$\frac{dR_1}{dt} = R_2Tk_2 + T\,OH\,k_s - R_1O_2k_1 - R_1OHk_t = 0$$

$$\frac{dR_2}{dt} = R_1O_2k_1 - R_2Tk_2 = 0$$

Substituting $R_1O_2k_1 = R_2Tk_2$

$$R_1OH\,k_t = T\,OH\,k_s$$

$$\therefore\ R_1 = T\,\frac{k_s}{k_t}$$

Substituting in (1)

$$\frac{-dO_2}{dt} = R_1O_2k_1 = \frac{Tk_sk_1O_2}{k_t}$$

i.e. $$\frac{-dO_2}{dt} = \frac{+dP}{dt} = k_1\,\frac{k_s}{k_t}\,(T)(O_2) \qquad (C)$$

Chain Termination by Reaction (8).

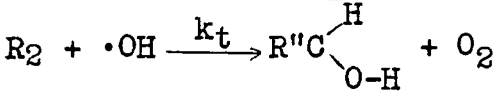
Assuming the chain cycle:-

Chain initiation $T + \cdot OH \xrightarrow{k_s} R_1 + H_2O$ (3)

Main chain $R_1 + O_2 \xrightarrow{k_1} R_2$ (1)

$R_2 + T \xrightarrow{k_2} P + R_1$ (2)

Chain termination



$R_2 + \cdot OH \xrightarrow{k_t} R''C{<}^{H}_{O-H} + O_2$ (8)

then in the steady state:-

$$\frac{dR_1}{dt} = R_2Tk_2 + OH\ T\ k_s - R_1O_2k_1 = 0$$

$$\frac{dR_2}{dt} = R_1O_2k_1 - R_2OHk_t + R_2Tk_2 = 0$$

Then $R_2Tk_2 + OH\ T\ k_s = R_2OHk_t + R_2Tk_2$

$$\therefore R_2 = \frac{T\ OH\ k_s}{OH\ k_t} = T\ \frac{k_s}{k_t}$$

Substituting in (2)

$$\frac{dP}{dt} = R_2Tk_2 = \frac{T^2k_sk_2}{k_t}$$

i.e. $\frac{-dO_2}{dt} = \frac{+dP}{dt} = k_2\ \frac{k_s}{k_t}\ (T)^2$ (D)

Thus, if chain termination is assumed to take place by reaction (8) then the rate expression (D) is in agreement with the experimental results of George and Robertson. The relationship (C), obtained by using reaction (7) as the chain termination reaction, accords with the results obtained by George and Robertson for the metal catalysed reaction. Chain termination by reaction (8) is also supported by chemical evidence; thus, exit gases from autoxidation processes invariably contain oxygen, and the results obtained from rapid low temperature decompositions of tetralin hydroperoxide (see Section IX) show that oxygen is liberated in approximately equivalent quantity to the αtetralol formed. αTetralol is one of the major reaction products, but apart from small-scale reaction with hydroxyl radicals to produce αtetralone, it is too stable to influence the reaction rate appreciably (Section III).

Chain initiation by reactions (5) and (6) combined with termination by reactions (7) and (8) do not give rate expressions which are in accord with George and Robertson's experimental results, although chain initiation by reaction (5) and chain termination by reaction (8) lead to a rate expression resembling that obtained by Medvedev and Podyapolskaya(93) for the initial period of low temperature oxidations. Thus, considering the reaction cycle:-

Chain initiation $\cdot OH + P \xrightarrow{k_s} H_2O + R_2$ (5)

Main chain $R_1 + O_2 \xrightarrow{k_1} R_2$ (1)

$R_2 + T \xrightarrow{k_2} P + R_1$ (2)

Chain termination $R_2 + \cdot OH \xrightarrow{k_t} R''C\begin{smallmatrix}\diagup H\\ \diagdown O\text{-}H\end{smallmatrix} + O_2$ (8)

in the steady state

$$\frac{dR_1}{dt} = R_2Tk_2 - R_1O_2k_1 + R_1OHk_t = 0$$

$$\frac{dR_2}{dt} = R_1O_2k_1 + OH\ P\ k_s - R_2Tk_2 = 0$$

$$\therefore \quad R_1 OH k_t = OH\, P\, k_s$$

$$\therefore \quad R_1 = P \frac{k_s}{k_t}$$

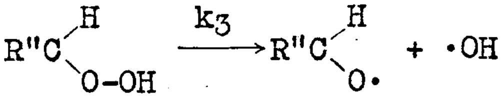
Substituting in reaction (1)

$$\frac{-dO_2}{dt} = \frac{dP}{dt} = k_1 O_2 P \frac{k_s}{k_t} \qquad (E)$$

Main Reaction Process.

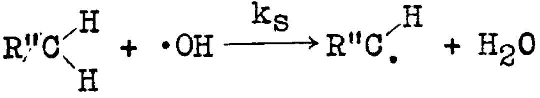
From the kinetic analysis given above the following chain cycle best represents the oxidation reaction in the steady state:-

Decomposition of the Hydroperoxide to produce Free Radicals.



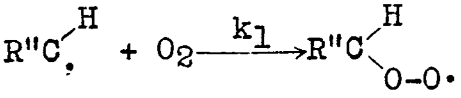
$$R''C\genfrac{}{}{0pt}{}{H}{O\text{-}OH} \xrightarrow{k_3} R''C\genfrac{}{}{0pt}{}{H}{O\cdot} + \cdot OH \qquad (3)$$

Chain Initiation Process.

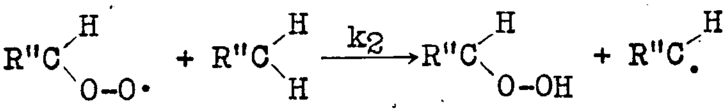


$$R''C\genfrac{}{}{0pt}{}{H}{H} + \cdot OH \xrightarrow{k_s} R''\overset{H}{C}\!\cdot + H_2O \qquad (4)$$

Main Oxygen Uptake Cycle.

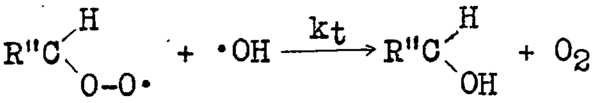


$$R''\overset{H}{C}\!\cdot + O_2 \xrightarrow{k_1} R''C\genfrac{}{}{0pt}{}{H}{O\text{-}O\cdot} \qquad (1)$$



$$R''C\genfrac{}{}{0pt}{}{H}{O\text{-}O\cdot} + R''C\genfrac{}{}{0pt}{}{H}{H} \xrightarrow{k_2} R''C\genfrac{}{}{0pt}{}{H}{O\text{-}OH} + R''\overset{H}{C}\!\cdot \qquad (2)$$

Chain Termination Process.



$$R''C\genfrac{}{}{0pt}{}{H}{O\text{-}O\cdot} + \cdot OH \xrightarrow{k_t} R''C\genfrac{}{}{0pt}{}{H}{OH} + O_2 \qquad (8)$$

The Inhibition of Autoxidation.

Results obtained in Section III confirmed Ivanov's(85) observation that inhibitors of autoxidations do not, in small concentration, act as rapid catalysts for the decomposition of the hydroperoxide. Inhibitors must function therefore by affecting the chain process by which the hydroperoxide is formed, and examples in which the radicals R_1 and R_2 are destroyed by interaction with the inhibitor will now be considered.

Inhibition by Destruction of the Hydrocarbon $(R''\underset{\bullet}{C}{}^{\diagup H})$ Radical

If chain termination occurs by interaction of R_1 with the inhibitor, then assuming the following chain cycle:-

Chain initiation	$T + \cdot OH \xrightarrow{k_s} \dot{R}_1 + H_2O$	(4)
Main chain	$R_1 + O_2 \xrightarrow{k_1} R_2$	(1)
	$R_2 + T \xrightarrow{k_2} P + R_1$	(2)
Chain termination	$R_1 + I \xrightarrow{k_i} \text{Inert Products}$	(9)

in the steady state

$$\frac{dR_1}{dt} = R_2Tk_2 + T\ OH\ k_s - R_1O_2k_1 + R_1Ik_i = 0$$

$$\frac{dR_2}{dt} = R_1O_2k_1 - R_2Tk_2 = 0$$

Then $R_1O_2k_1 = R_2Tk_2$ and $T\ OH\ k_s = R_1Ik_i$

$$\therefore R_1 = \frac{T\ OH\ k_s}{Ik_i}$$

Substituting in Reaction (1)

$$\frac{-dO_2}{dt} = R_1O_2k_1 = \frac{k_1O_2T\ OHk_s}{Ik_i}$$

$$\text{i.e. } \frac{-dO_2}{dt} = \frac{+dP}{dt} = \frac{k_1k_s}{k_i}\ \frac{(T)(OH)(O_2)}{(I)} \qquad (F)$$

Since both the uninhibited and inhibited oxidations have the same kinetic characteristics

$$k_o \sim (T)^2(O_2)^o$$

$$R_i \sim (T)^2(O_2)^o$$

it appears highly probable that the inhibitor must remove the same radical as the chain stopper, that is the peroxide radical.

Inhibition by Destruction of the Peroxide $\left(R''C\begin{smallmatrix}\diagup H\\ \diagdown O\text{-}O\cdot\end{smallmatrix}\right)$ Radical.

If chain termination occurs by reaction of R_2 with the inhibitor, then assuming the following chain cycle:-

Chain initiation	$T + \cdot OH \xrightarrow{k_s} R_1 + H_2O$	(4)
Main chain	$R_1 + O_2 \xrightarrow{k_1} R_2$	(1)
	$R_2 + T \xrightarrow{k_2} P + R_1$	(2)
Chain termination	$R_2 + I \xrightarrow{k_i} \text{Inert Products}$	(10)

in the steady state

$$\frac{dR_1}{dt} = R_2Tk_2 + T\ OH\ k_s - R_1O_2k_1 = 0$$

$$\frac{dR_2}{dt} = R_1O_2k_1 - R_2Tk_2 + R_2Ik_i = 0$$

$$\therefore R_2Tk_2 + T\ OH\ k_s = R_2Tk_2 + R_2Ik_i$$

$$\therefore R_2 = \frac{T\ OH\ k_s}{Ik_i}$$

Substituting Reaction (2)

$$\frac{dP}{dt} = RTk_2 = \frac{k_sk_2}{k_i}\ \frac{(T)^2OH}{I}$$

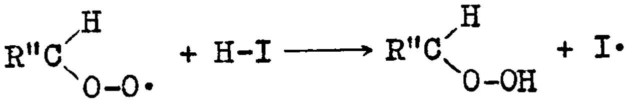
$$\text{i.e. } +\frac{dP}{dt} = \frac{-dO_2}{dt} = \frac{k_sk_2}{k_i}\ \frac{(T)^2(OH)}{(I)} \qquad (G)$$

Both reactions (9) and (10) give expressions for the reaction rate which are proportional to the hydroxyl radical concentration and therefore to the hydroperoxide concentration, and, in consequence, correspond to the initial stage of the reaction when it is autocatalytic. Chain termination by interaction of R_2 with the inhibitor gives a rate expression (G) involving $(T)^2$ and is in better agreement with observed results for the thermal oxidation than is (F).

The rate expression (F) is of first order with respect to both hydrocarbon and oxygen concentrations. Rate dependency upon oxygen pressure only occurs with tetralin and ethyl linoleate at very low pressures, though George has shown that the benzoyl peroxide catalysed oxidation of tetralin is much more susceptible to pressure variation. Such a dependency upon oxygen pressure indicates chain stopping by destruction of R_1 (Reactions (7) and (9)), and if these reactions take place in preference to (8) and (10) then the ratio $\frac{(R_1)}{(R_2)}$ must be high.

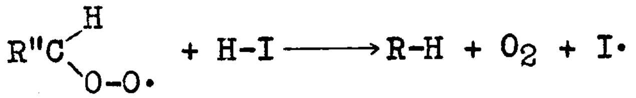
Since the chain length of the reaction is large, then $R_1O_2k_1 \sim R_2Tk_2$, and if $\frac{(O_2)}{(T)}$ is decreased, $\frac{R_1}{R_2}$ will be increased which is the relationship expected from the theory considered above.

Inhibition by destruction of peroxide radicals may occur by the reaction:-



$$R''C\begin{matrix}H\\O\text{-}O\cdot\end{matrix} + H\text{-}I \longrightarrow R''C\begin{matrix}H\\O\text{-}OH\end{matrix} + I\cdot \qquad (11)$$

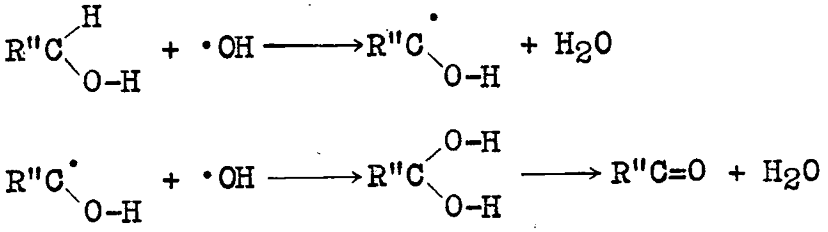
where I· is a resonance stabilised radical which is incapable of attacking the C-H bond. The fact that this type of inhibitor does not function by the destruction of the peroxide molecule (Section III) substantiates this theory. An alternative reaction would be:-



$$\mathrm{R''C}\begin{matrix}\diagup \mathrm{H}\\ \diagdown \mathrm{O{-}O\cdot}\end{matrix} + \mathrm{H{-}I} \longrightarrow \mathrm{R{-}H} + \mathrm{O_2} + \mathrm{I\cdot} \qquad (12)$$

and this may well occur in cases of inhibition by surfaces or metallic radicals by provision of an electron.

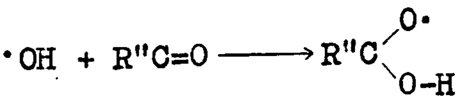
Products of oxidation may function as inhibitors as has been shown in the case of o.phenol butyric acid. α Tetralol has but little effect on the reaction, although the quantity of hydroxyl radicals available for chain initiation will be decreased by the following reactions:-



$$\mathrm{R''C}\begin{matrix}\diagup \mathrm{H}\\ \diagdown \mathrm{O{-}H}\end{matrix} + \cdot\mathrm{OH} \longrightarrow \mathrm{R''\dot{C}}\begin{matrix}\\ \diagdown \mathrm{O{-}H}\end{matrix} + \mathrm{H_2O}$$

$$\mathrm{R''\dot{C}}\begin{matrix}\\ \diagdown \mathrm{O{-}H}\end{matrix} + \cdot\mathrm{OH} \longrightarrow \mathrm{R''C}\begin{matrix}\diagup \mathrm{O{-}H}\\ \diagdown \mathrm{O{-}H}\end{matrix} \longrightarrow \mathrm{R''C{=}O} + \mathrm{H_2O}$$

which occur on a small scale (Section V). Corresponding attack on the ketone by the hydroxyl radical:-



$$\cdot\mathrm{OH} + \mathrm{R''C{=}O} \longrightarrow \mathrm{R''C}\begin{matrix}\diagup \mathrm{O\cdot}\\ \diagdown \mathrm{O{-}H}\end{matrix}$$

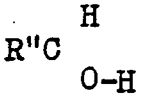
appears unlikely since the corresponding carboxylic acid was not isolated.

If the general case of autoxidation is considered and inhibition takes place by reaction (11), then assuming the chain sequence:-

Chain initiation $T + \cdot OH \xrightarrow{k_s} R_1 + H_2O$ (4)

Main chain $R_1 + O_2 \xrightarrow{k_1} R_2$ (1)

$R_2 + T \xrightarrow{k_2} P + R_1$ (2)

Chain termination $R_2 + \cdot OH \xrightarrow{k_t}$  $+ O_2$ (8)

$$R_2 + \cdot OH \xrightarrow{k_t} R''C\overset{H}{\underset{O-H}{}} + O_2 \quad (8)$$

$R_2 + HI \xrightarrow{k_i} RH + O_2 + I\cdot$ (12)

in the steady state

$$\frac{dR_1}{dt} = R_2Tk_2 + T\ OH\ k_s - R_1O_2k_1 = 0$$

$$\frac{dR_2}{dt} = R_1O_2k_1 - TR_2k_2 - R_2OHk_t - R_2HIk_i = 0$$

$$\therefore T\ OH\ k_s = R_2OHk_t + R_2HIk$$

$$R\ (OHk_t + HIk_i) = T\ OH\ k_s$$

$$R_2 = \frac{T\ OH\ k_s}{OHk_t + HIk_i}$$

Substituting in Reaction (2)

$$\frac{dP}{dt} = R_2Tk_2 = \frac{(T)^2(OH)k_sk_2}{(OH)k_t + (HI)k_i} \qquad (H)$$

If inhibition takes place by reaction (11), then assuming the same reaction cycle

$$\frac{dR_1}{dt} = R_2Tk_2 + T\ OH\ k_s - R_1O_2k_1 = 0$$

$$\frac{dR_2}{dt} = R_1O_2k_1 - R_2Tk_2 - R_2OH\ k_t - R_2HIk_i$$

$$\therefore T\ OH\ k_s = R_2OHk_s + R_2HIk_i$$

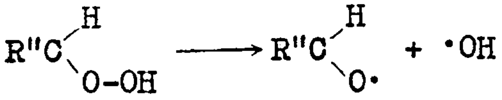
$$R_2 = \frac{T\ OH\ k_s}{OHk_t + HIk_i}$$

Substituting in reactions (2) and (11)

$$\frac{dP}{dt} = R_2T\ k_s + R_2HIk_i$$

$$\frac{dP}{dt} = \frac{(T)(OH)k_s[(T)k_2 + (HI)k_i]}{(OH)k_t + (HI)k_i} \qquad (I)$$

When the concentration of the inhibitor is small in comparison with the concentration of the hydroxyl radical, i.e. when sufficient hydroperoxide has accumulated in the system to generate a steady supply of radicals by the reaction



or sufficient inhibitor has been consumed by participation in reactions of type (11) and (12), then equations (H) and (I) simplify to (D):-

$$+\frac{dP}{dt} = k_2\ \frac{k_s}{k_t}\ (T)^2$$

corresponding to the steady state of the oxidation.

During the autocatalytic stage of the oxidation, the peroxide concentration is comparatively small, and since $d(OH) = (P)k_3$, equation (H) reduces to:-

$$\frac{dP}{dt} = \frac{(T)^2(OH)k_sk_2}{(HI)k_i} \qquad (J)$$

and equation (I) to:-

$$\frac{dP}{dt} = \frac{(T)(OH)k_s[(T)k_2 + (HI)k_i]}{(HI)k_i} \qquad (K)$$

George, Rideal and Robertson(13) derived the following expression for the rate of chain initiation of the strongly inhibited oxidation of tetralin:-

$$a = \frac{I_o}{t_i}$$

where a = rate of chain initiation

I_o = initial inhibitor concentration

t_i = induction period.

It follows that the induction period $(t_i) = \frac{I_o}{a}$. From reaction (4) the rate of chain initiation = $k_s(OH)(T)$. Substituting $a = k_s(OH)(T)$,

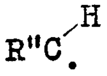
$$\text{the induction period} = \frac{I_o}{k_s(OH)(T)} \qquad (L)$$

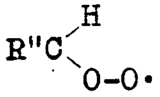
which is in agreement with George and Robertson's experimental results.

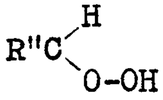
The salient features of the mechanisms considered are summarised in Table XXIII. In all cases the main chain is accepted as:-

$$R_1 + O_2 \xrightarrow{k_1} R_2 \qquad (1)$$

$$R_2 + T \xrightarrow{k_2} P + R_1 \qquad (2)$$

and R_1 =

$R''C(H)\cdot$

R_2 =

$R''C(H)O{-}O\cdot$

P =

$R''C(H)O{-}OH$

T = Hydrocarbon

HI = Inhibitor

Table XXIII.

Uninhibited Oxidation

Chain Initiation	Chain Termination	Rate
(4) $\cdot OH + T \xrightarrow{k_s} R_1 + H_2O$	(7) $R_1 + \cdot OH \xrightarrow{k_t} ROH$	(C) $\frac{dP}{dt} = \frac{k_1 k_s}{k_t}(T)(O_2)$
(4) $\cdot OH + T \xrightarrow{k_s} R_1 + H_2O$	(8) $R_2 + \cdot OH \xrightarrow{k_t} ROH + O_2$	(D) $\frac{dP}{dt} = k_2 \frac{k_s}{k_t}(T)^2$
(5) $\cdot OH + P \xrightarrow{k_s} H_2O + R_2$	(8) $R + \cdot OH \xrightarrow{k_t} ROH + O_2$	(E) $\frac{dP}{dt} = k_1(O_2)(P)\frac{k_s}{k_t}$

Inhibited Oxidation

Chain Initiation	Chain Termination	Rate
(4) $\cdot OH + T \xrightarrow{k_s} R_1 + H_2O$	(9) $R_1 + HI \xrightarrow{k_i} Inerts$	(F) $\frac{dP}{dt} = \frac{k_1 k_s (T)(OH)(O_2)}{k_i \quad (HI)}$
(4) $\cdot OH + T \xrightarrow{k_s} R_1 + H_2O$	(10) $R_2 + HI \xrightarrow{k_i} Inerts$	(G) $\frac{dP}{dt} = \frac{k_s k_2}{k_i} \frac{(T)^2 (OH)}{(HI)}$

(Cont'd)

Table XXIII (Cont'd)

General Case

Chain Initiation	Chain Termination	Rate
(4) $\cdot OH + T \xrightarrow{k_s} R_1 + H_2O$	(8) $R_2 + \cdot OH \xrightarrow{k_t} R{-}OH + O_2$ (11) $R_2 + HI \xrightarrow{k_i} P + I\cdot$	(H) $\frac{dP}{dt} = \frac{(T)^2 (OH) k_s k_2}{(OH)k_t + (HI)k_i}$
(4) $\cdot OH + T \xrightarrow{k_s} R_1 + H_2O$	(8) $R_2 + \cdot OH \xrightarrow{k_t} R{-}OH + O_2$ (12) $R_2 + HI \xrightarrow{k_i} R{-}H + O_2 + I\cdot$	(I) $\frac{dP}{dt} = \frac{(T)(OH)k_s[(T)k_2 + (HI)k_i]}{(OH)k_t + (HI)k_i}$

Initial Stages of Oxidation (i.e. P is small)

Chain Initiation	Chain Termination	Rate
(4) $\cdot OH + T \xrightarrow{k_s} R_1 + H_2O$	(8) $R_2 + \cdot OH \xrightarrow{k_t} R{-}OH + O_2$ (11) $R_2 + HI \xrightarrow{k_i} P + I\cdot$	(J) $\frac{dP}{dt} = \frac{(T)^2(OH)k_s k_2}{(HI)k_i}$
(4) $\cdot OH + T \xrightarrow{k_s} R_1 + H_2O$	(8) $R_2 + \cdot OH \xrightarrow{k_t} R{-}OH + O_2$ (12) $R_2 + HI \xrightarrow{k_i} R{-}H + O_2 + I\cdot$	(K) $\frac{dP}{dt} = \frac{(T)(OH)k_s[(T)k_2 + (HI)k_i]}{(HI)k_i}$

Induction Period $= \frac{(HI_0)}{k_s(OH)(T)}$ (L)

The evidence which has been obtained of the participation of free radicals in the oxidation renders George and Robertson's energy chain theory highly improbable. Their conclusion that a free radical mechanism, based upon mutual chain termination reactions, was not compatible with the observed kinetic results must be rejected on the basis of the mechanisms that have been postulated in this Section for the oxidation and which give rate expressions in accordance with the observed results (Table XXIII - D, G, H, I, J, K, L).

Conclusions.

The low temperature liquid phase oxidation of tetralin proceeds by a free radical chain mechanism. Chain initiation in the pure hydrocarbon occurs either as the result of the presence of sub-analytical quantities of the hydroperoxide or by adventitious catalysis (e.g. by a surface activation). After an induction period during which the hydroperoxide accumulates in the system and the greater part of the oxygen absorbed is accounted for as hydroperoxide, the reaction attains a steady state. The hydroperoxide which is formed decomposes to produce free radicals which either undergo an intramolecular reaction to produce α tetralone or else participate in a series of chain initiation or termination reactions. During the steady state reaction, chain initiation occurs by interaction of the hydrocarbon with hydroxyl radicals produced by the decomposition of the hydroperoxide, and chain termination occurs by interaction of the hydroxyl and peroxide radicals. The rate of reaction gradually decreases in the later stages of the oxidation because of the decrease in the concentration of the hydrocarbon available for oxidation and the presence of inhibitors (e.g. o.phenol butyric acid) among the reaction products.

Inhibition occurs when peroxide radicals are destroyed by interaction with the inhibitor, thus breaking the propagation chain.

Although in many other examples of liquid phase hydrocarbon oxidations such well-defined stages of reaction cannot be clearly recognised because of the instability of the intermediate hydroperoxide, the fact that Larsen and co-workers(110) have shown that the liquid phase oxidation of higher paraffins, cycloparaffins, and alkyl benzenes in no way differs from that of tetralin suggests that the general applicability of the mechanisms suggested would be unaffected.

VIII. THE EFFECT OF HALOGEN COMPOUNDS ON THE AUTOXIDATION OF TETRALIN.

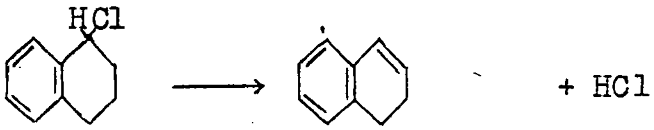
Preliminary results reported in Section IV. and listed in Table IX. showed that N-Halogen-imides were excellent catalysts for the autoxidation of tetralin, and gave strong support for the theory that positive halogen compounds could undergo homolytic bond fission. An examination of the products obtained by the reaction of two typical N-halogen imides (N-2:4-trichlorobenzanilide and N-2:4:6-tetrachlorobenzanilide) with tetralin gave chemical evidence supporting these kinetic results.

0.1 mol. of the N-chloro-imides were dissolved in 0.5 mol. of pure tetralin and refluxed with 75 mls. of carbon tetrachloride (which had been purified by distillation) for two hours in an atmosphere of nitrogen. A small quantity of acid fumes were evolved and testing with silver nitrate showed them to be hydrogen chloride. On cooling the mixture white crystals were deposited and after the removal of the carbon tetrachloride by distillation under reduced pressure further heavy deposition took place. The residual tetralin solution was cooled to 0°C. and then filtered. The crystalline product was lightly washed with alcohol and then recrystallised from the same solvent. The purified product from the N-2:4-trichlorobenzanilide reaction melted at 117°C. which was identical with the melting point of dichlorobenzanilide. Similarly, the purified product from the N-2:4:6-tetrachlorobenzanilide reaction gave a melting point identical to that of trichlorobenzanilide, 174°C. In both cases the yield of the chlorobenzanilides was almost theoretical (25 gms and 29 gms).

The residual tetralin solutions were fractionally distilled at 15 mms giving a fraction of boiling point (a) 86°C. which consisted mainly of tetralin, (b) 120°C. from which hydrogen chloride was evolved during distillation, and (c) 220-230°C., a viscous oil which had a pronounced blue fluorescence in ultra-violet light.

Fraction (a), unlike pure tetralin, gave a blue colouration with alcoholic sodium hydroxide and at 0°C. immediately decolourised a solution of bromine in chloroform without HBr evolution. After the removal of chloroform from the brominated sample under reduced pressure, and storage of the residual solution at -10°C. crystals were deposited which, after purification by recrystallisation from alcohol gave a melting point identical to the dibromide of 1:2-dihydronaphthalene (73°C.).

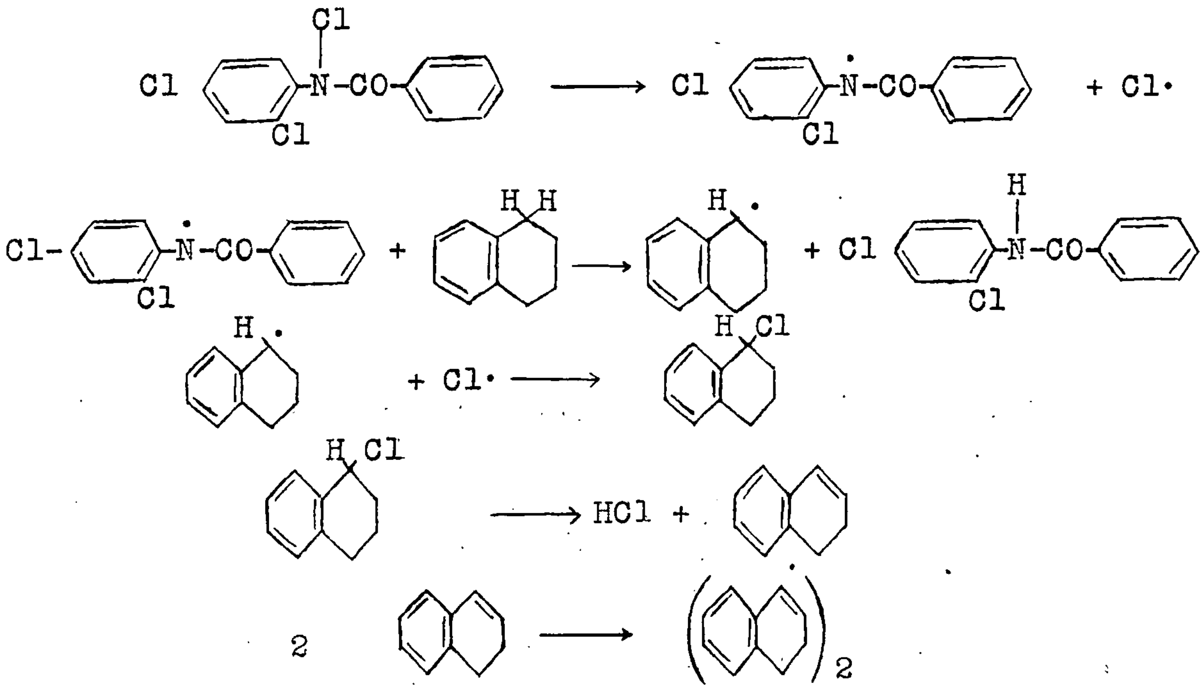
Fraction (b) on heating at 190°C. in air evolved hydrogen chloride and the residual solution gave the colour reaction and the bromine addition product typical of 1:2-dihydronaphthalene. Bamberger(186) has shown that tetralyl chloride has a strong tendency to undergo decomposition during distillation with the production of hydrogen chloride and dihydronaphthalene:-



Attempts to hydrolyse fraction (b) to α tetralol with potassium carbonate were not successful.

Fraction (c) was purified by chromatographing a benzene solution through an alumina column in ultra-violet light. The product analysed C 91.7%, H 7.54% which corresponds to the dimer of 1:2-dihydronaphthalene (theoretical C 92.3%, H 7.69%) which Bamberger has reported to be produced during the decomposition of tetralyl chloride.

The sequence of the reaction between N-2:4-trichlorobenzanilide and tetralin may thus be represented by:-


Cl
Cl
N-CO
Cl
Cl
Cl
N-CO
+ Cl·
Cl-
N-CO
Cl
+
H H
H .
+ Cl
H
N-CO
Cl
H .
+ Cl·
H Cl
H Cl
HCl +
2
2

The effect of the addition of positive C-halogen compounds and alkyl, acyl and aryl halides on the autoxidation of tetralin was investigated in the static apparatus at 76°C. using 1 gm. of the compound under investigation and 30 mls. of tetralin. The halogen compounds were purified by distillation or recrystallisation, and in the case of benzyl chloride, to obviate the possibility of catalysis by traces of benzaldehyde, the material was prepared from aldehyde-free (bisulphite washed) benzyl alcohol by the action of concentrated hydrochloric acid. Results obtained are shown in Tables XXIV and XXV. The effect of the addition of typical unhalogenated parent compounds are shown for comparison.

Table XXIV.

Catalysis of the Autoxidation of Tetralin by Positive C-Halogen Compounds.

Substance Added	Oxygen Uptake mls/15 mins			
	Time from Start of Autoxidation			
	0-15 mins	15-30 mins	45-60 mins	105-120 mins
Tetralin (Blank)	0.5	0.7	0.9	1.4
Diethyl-α-bromo malonate	21	19	15	11
Chloropicrin	14	20	19	14
α-Bromobenzyl cyanide	15	14	12	10
p.Phenyl-phenacyl chloride	9	15	13	-
Bromo-nitroform	14	13	7	6

(Cont'd)

Table XXIV. (Cont'd)

Catalysis of the Autoxidation of Tetralin by Positive C-Halogen Compounds.

Substance Added	Oxygen Uptake mls/15 mins			
	Time from Start of Autoxidation			
	0-15 mins	15-30 mins	45-60 mins	105-120 mins
Monochloroacetone	3	8	14	14
1-Chloro-1-nitropropane	2	4	7	10
Tri-ω-bromoquinaldine	3	6	10	11
Chloro-trinitromethane	5	5	5	3
Phenyl-α-bromoacetamide	2	5	8	7
p.Nitro-α-chloroacetophenone	2	3	4	5
Phenyl-α-chloromethylsulphone	2	3	3	-
2-Chloro-2-nitropropane	1	1	1	-
Sym. Dichloroacetone	1	1	1	-
(Comparison Substances)				
Diethyl malonate	1	1	1	-
Ethyl phenylacetate	1	2	2	-

Figure XXV.

THE EFFECT OF POSITIVE HALOGEN COMPOUNDS ON THE OXIDATION OF TETRALIN.

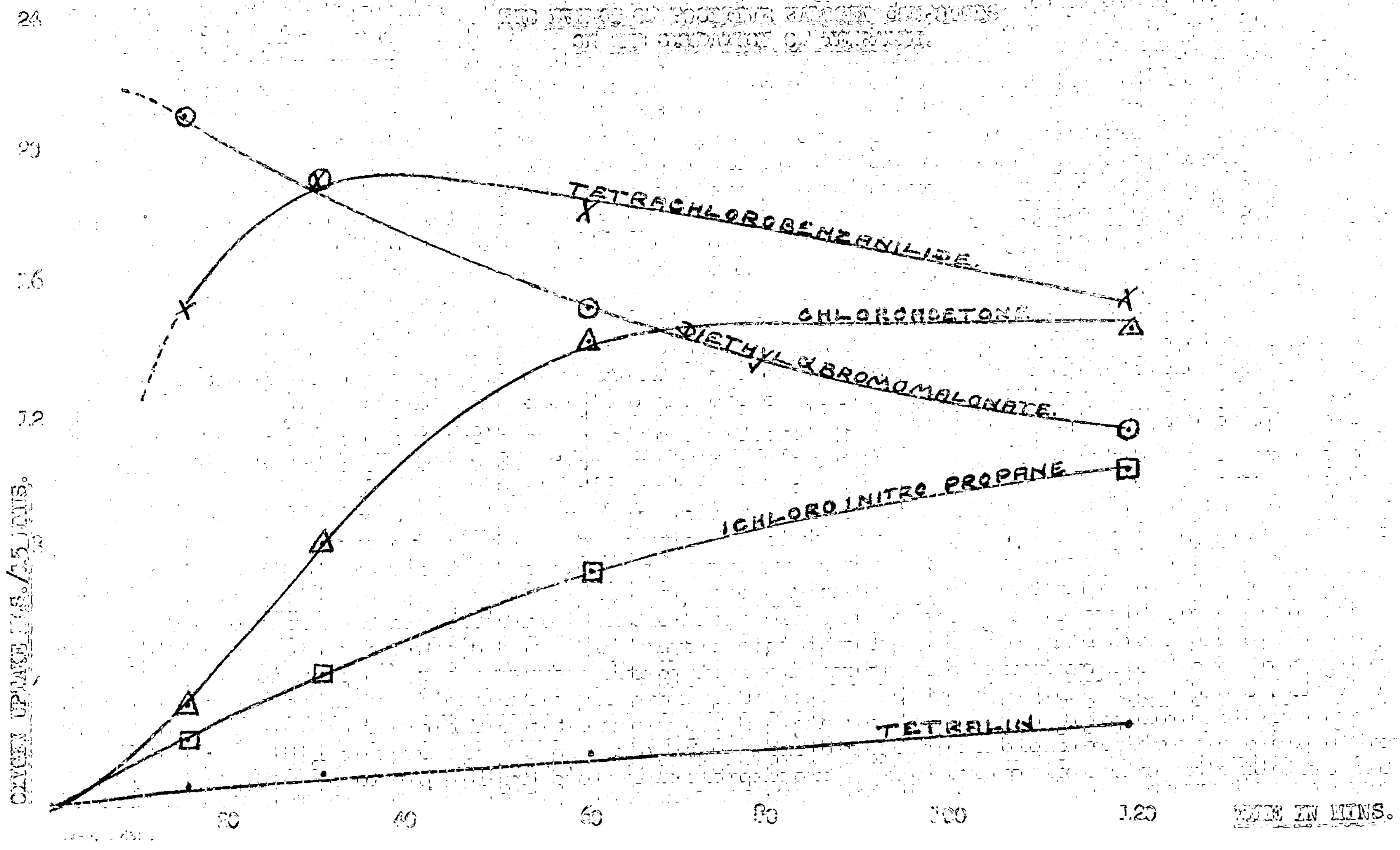


Table XXV.

Catalysis of the Autoxidation of Tetralin by Alkyl, Acyl and Aryl Halides.

Substance Added	Oxygen Uptake mls/15 mins			
	Time from Start of Autoxidation			
	0-15 mins	15-30 mins	45-60 mins	105-120 mins
Tetralin (blank)	0.5	0.7	0.9	1.4
Benzyl bromide	9	15	17	14
Benzyl chloride	3	6	7	11
Ethyl bromoacetate	11	14	12	11
Ethyl dichloroacetate	1	4	12	14
Triphenylmethyl chloride	2	2	3	-
Cyclohexyl chloride	2	3	3	-
α-Chloronaphthalene	3	3	4	-
Chlorobenzene	2	2	2	-
Benzoyl chloride	1	1	1	-
Ethyl chloroacetate	1	1	1	-
Hexachloroethane	2	3	3	-

It can be seen that both types of halogen compounds were catalysts for the autoxidation of tetralin whereas the corresponding halogen free compounds were inactive.

Typical examples of catalysis by halogen compounds are illustrated in Figure XXVI.

Substances like chloropicrin and diethyl-bromomalonate which react very rapidly with potassium iodide in acetic acid solution resembled the N-halogen-imides in being active catalysts for the autoxidation. They brought about an immediate oxygen absorption which gradually decreased as the supply of chain initiators became smaller and smaller. The catalysis could, therefore, be represented as:-

(1) a homolytic fission of the halogen compound

$$R{\cdot}X \longrightarrow R{\cdot} + X{\cdot}$$

(2) catalysis of the main tetralin oxidation cycle

$$R{\cdot} + C_{10}H_{12} \longrightarrow RH + C_{10}H_{11}{\cdot} \qquad (1)$$

$$C_{10}H_{11}{\cdot} + O_2 \longrightarrow C_{10}H_{11}\text{-}O\text{-}O{\cdot} \qquad (2)$$

$$C_{10}H_{11}\text{-}O\text{-}O{\cdot} + C_{10}H_{12} \longrightarrow C_{10}H_{11}{\cdot}O\text{-}OH + C_{10}H_{11} \qquad (3)$$

Less active halogen compounds which react only slowly, if at all, with potassium iodide in acetic acid solution were also catalysts of the autoxidation though the immediate catalysis was much less marked. Such compounds promoted an initial oxygen absorption which was greater than that of the pure hydrocarbon and which gradually increased with time. 1-Chloro-1-nitropropane and benzyl chloride are examples of this type (see Figure XXVI). This behaviour would be typical of a substance which underwent very slow homolytic fission to produce chain initiators and superimposed this effect upon the normal catalysis produced by the hydroperoxide accumulating in the system.

The homolysis of such halides to produce free radical initiators by a unimolecular decomposition:-

$$R\text{-}X \longrightarrow R\cdot + X\cdot \qquad (4)$$

is not the only mechanism by which this catalysis could take place.

If other radicals (Y•) were present in the system, halogen atom extraction could first take place by the reaction:-

$$Y\cdot + RX \longrightarrow YX + R\cdot \qquad (5)$$

Thus an active free hydrocarbon radical would be produced which would be capable of initiating the main oxidation chain process as in reactions (1), (2) and (3). If reaction (5) occurs more rapidly than the normal adventitious catalysis of reaction (1) then the addition of a halide to tetralin will accelerate the autoxidation. The reaction:-

$$C_{10}H_{11}\cdot + R\text{-}Br \longrightarrow C_{10}H_{11}Br + R\cdot$$

may also occur, but if it is slower than reaction (2) then most of tetralin will be autoxidised and not brominated, although such a competitive chain reaction may well prevent a high level of oxygen absorption being attained.

It is probable that catalysis of the autoxidation by the less active type of halogen compound occurs by the bimolecular mechanism (5) because the presence of a minute trace of tetralin hydroperoxide in the tetralin used would provide the radicals Y• to start off the main reaction chain, and this is substantiated by the fact that Hey(187) was unable to obtain evidence of the occurrence of homolytic bond fission in triphenyl methyl chloride. Support for such a hypothesis is given by the observation of Kharasch and Mayo(188) that bromoacetoacetic ester (which is a typical compound of this group) is stable except in the presence of traces of oxygen or peroxides. Peroxide catalysed addition and substitution processes involve such reactions as (5) and further support for the hypothesis outlined above is the fact that Karrer and Schmid(189) have shown that bromination in the α methylenic position using N-bromo-succinimide is accelerated to a marked extent by the addition of a little dibenzoyl peroxide to the mixture.

A study of the products of reactions of halogen compounds of this type with tetralin gave evidence supporting the kinetic results. 0.1 mol. of benzyl bromide, 0.5 mol. of tetralin, and 75 mls. of dry carbon tetrachloride were refluxed under nitrogen for 8 hours. The mixture gradually became yellow and acid vapours were evolved which, on testing with silver nitrate, proved to be hydrogen bromide. After the removal of the carbon tetrachloride by distillation the residual solution was distilled at 15 mms. The following fractions were obtained: (a) B.P. 84-88°C., a mixture of tetralin and unchanged benzyl bromide which gave positive tests for dihydronaphthalene, decolourising a solution of bromine in chloroform at 0°C., and giving a blue colouration with alcoholic sodium hydroxide, (b) B.P. 140°C. which evolved HBr during distillation and, on heating in air at 190°C., evolved further HBr leaving a residual solution which gave positive tests for dihydronaphthalene, and (c) B.P. approx. 220°C., a small quantity of a viscous liquid which fluoresced in ultra-violet light. Thus, as with the chlorimides, halogenation of the tetralin took place, and the tetralyl bromide which was formed decomposed to produce HBr, dihydronaphthalene and dihydronaphthalene dimer.

IX. THE METAL CATALYSED LIQUID PHASE OXIDATION OF TETRALIN.

Metal salts of the naphthalene carboxylic acids found in petroleum have been used extensively as driers and oxidation catalysts(190), and cobalt naphthenate was selected as a suitable catalyst for the oxidation of tetralin.

Materials.

Tetralin and Tetralin Hydroperoxide.

Prepared as in Section II.

Cobalt Naphthenate.

Cobalt naphthenate was prepared by the action of excess naphthenic acid on basic cobalt carbonate. Basic cobalt carbonate was prepared by the addition of ammonium carbonate solution to cobalt nitrate, and after isolation by filtration, was slowly added in stoichiometric quantity (as estimated from the acid value) to naphthenic acid at 90°C. during a two-hour period. The mixture was then heated overnight on a steam bath and the product employed as a 1% solution in chlorobenzene.

Apparatus.

As described in Section II.

Investigation of Hydroperoxide Formation and Oxygen Uptake.

The effect of the addition of varying quantities of cobalt naphthenate on the rate of formation of the hydroperoxide at 76°C. was investigated in the flow apparatus. Varying quantities (0.375 ml. to 5 ml.) of a 1% solution of

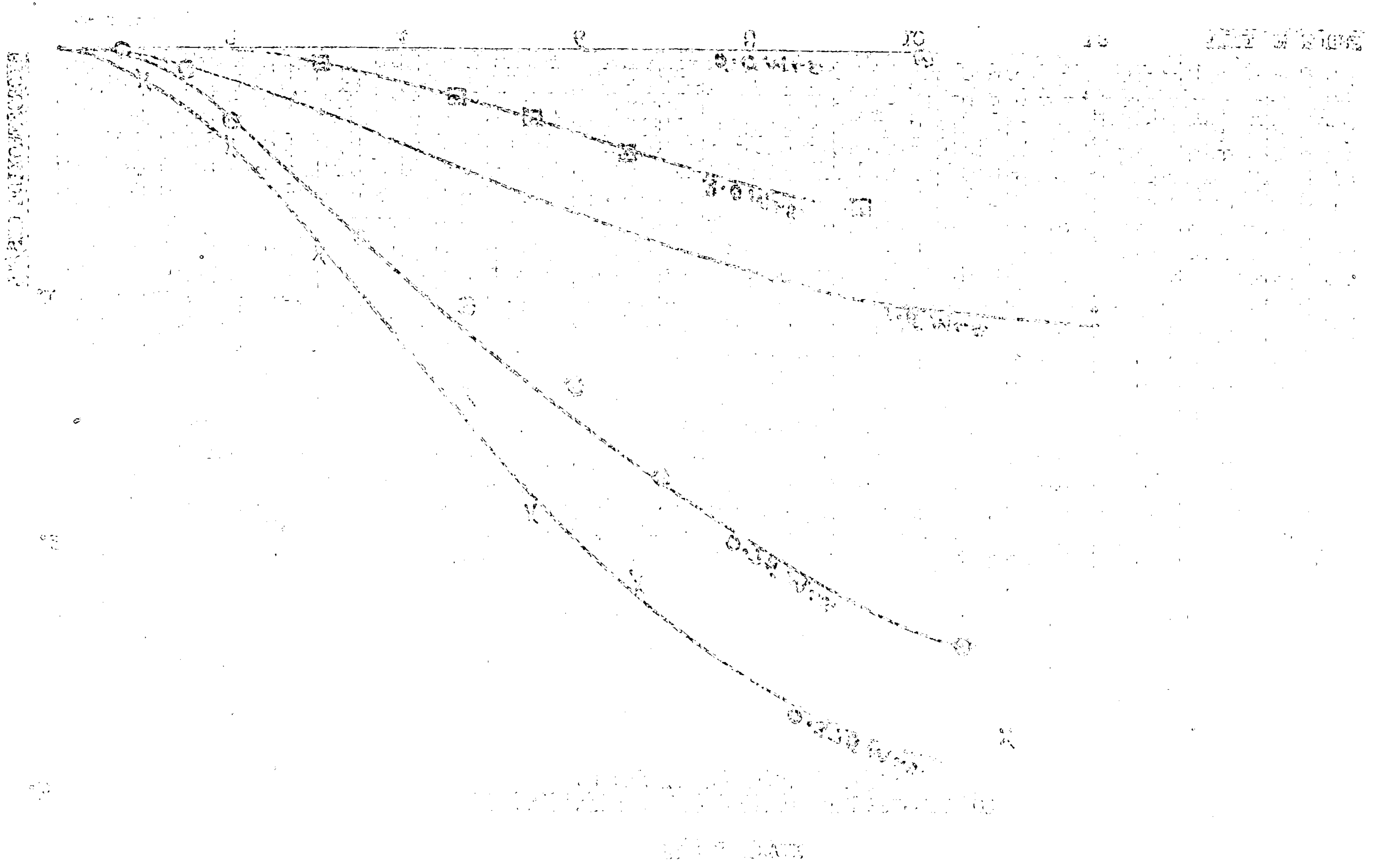
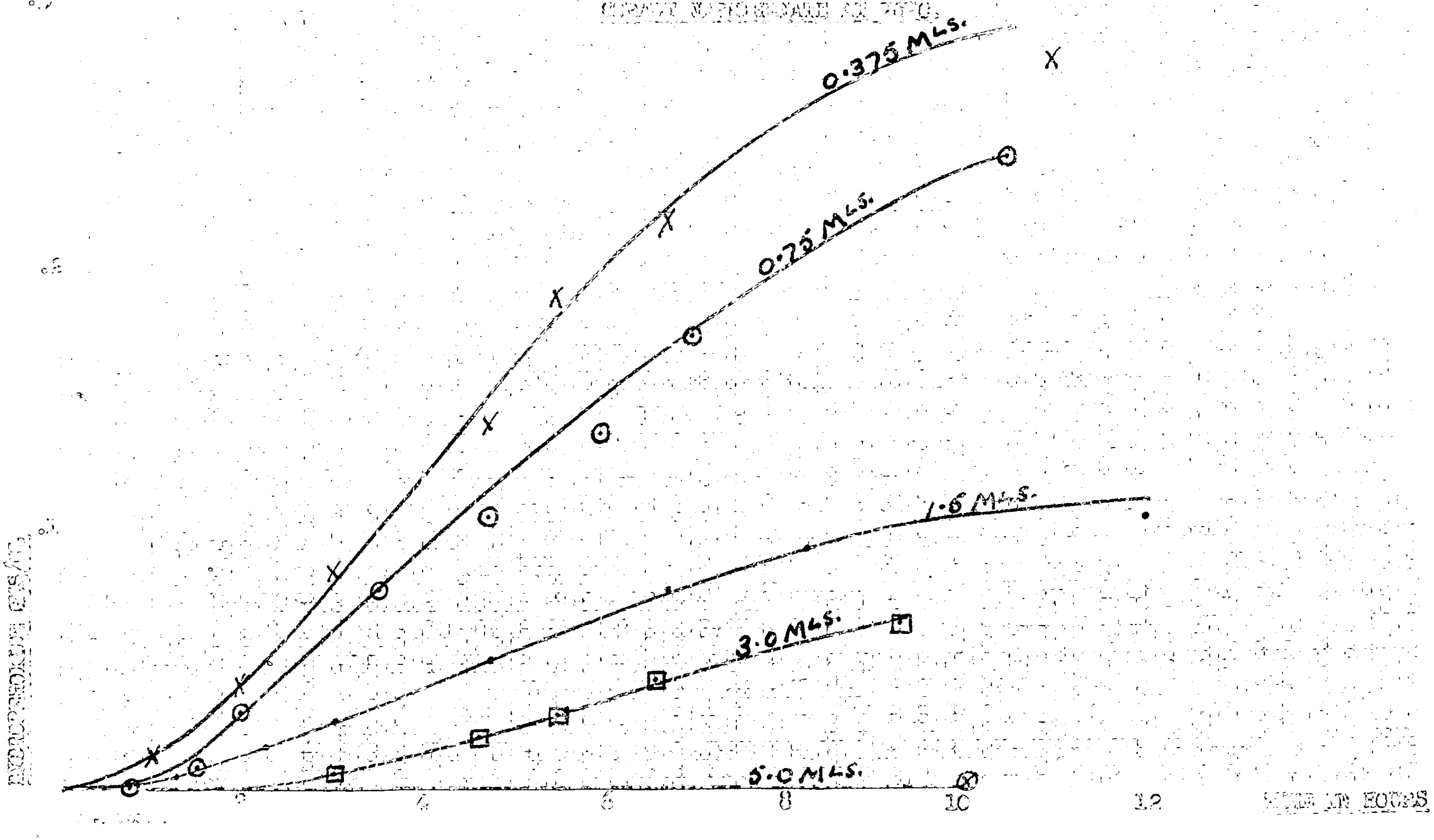

2
4
6
8
10
9.0 Wt-%
3.0 Wt-%
0.59 Wt-%

FIGURE XXVI

THE OXIDATION OF TETRALIN IN THE PRESENCE OF COBALT NAPHTHENATE AT 75°C.



cobalt naphthenate in chlorobenzene was added to 30 mls. of tetralin and the hydroperoxide content estimated at periodic intervals. Results are shown in Table XXVI and illustrated in Figure XXVII.

Table XXVI.

The Oxidation of Tetralin in the Presence of Cobalt Naphthenate.

0.375 mls. Cobalt Naphthenate Solution								
Time after start of oxidation(hrs)	1.0	2.0	3.0	4.75	5.5	6.75	11.0	
Hydroperoxide (gms./ml.)	.012	.039	.081	.136	.185	.212	.273	
0.75 mls. Cobalt Naphthenate Solution								
Time after start of oxidation(hrs)	0.66	1.5	2.0	3.5	4.75	6.0	7.0	10.5
Hydroperoxide (gms./ml.)	.001	.008	.031	.076	.101	.134	.171	.237
1.5 mls. Cobalt Naphthenate Solution								
Time after start of oxidation(hrs)	0.75	1.25	2.25	3.0	4.75	6.75	8.25	12.0
Hydroperoxide (gms./ml.)	.001	.004	.016	.026	.047	.074	.083	.099
3.0 mls. Cobalt Naphthenate Solution								
Time after start of oxidation(hrs)	1.0	2.0	3.0	4.5	5.5	6.6	9.3	
Hydroperoxide (gms./ml.)	-	-	.004	.020	.028	.041	.062	
5.0 mls. Cobalt Naphthenate Solution								
Time after start of oxidation(hrs)	1.0	2.0	3.0	6.0	8.0	10.0		
Hydroperoxide (gms./ml.)	-	-	-	-	-	-		

Figure XXVII shows that as the quantity of added catalyst was increased, the rate of hydroperoxide formation gradually decreased until, when 5 mls. of cobalt naphthenate solution had been added, the formation of the hydroperoxide could not be observed.

Approximate measurements of oxygen uptake with the flow apparatus showed that oxygen absorption was still taking place at the high catalyst concentrations. It therefore appeared that in the catalysed oxidation, unlike the thermal oxidation, the rate of hydroperoxide formation in the initial stages of the reaction could not be taken as an index of the rate of the reaction which would be better measured in terms of oxygen uptake.

The rate of oxygen uptake during the cobalt naphthenate catalysed oxidation was measured in the static apparatus and, as shown in Table XXVII, there was a marked increase over the rate obtained in the thermal oxidation. Analysis of the solution for hydroperoxide content showed that appreciable quantities of the oxygen absorbed could not be accounted for as hydroperoxide, and the presence of water in the reaction flask indicated that hydroperoxide decomposition was occurring.

Table XXVII.

The Oxidation of Tetralin in the Presence of Cobalt Naphthenate.

	Oxygen Uptake mls./15 minutes						
	Time after Start of Oxidation						
	15 mins	30 mins	45 mins	75 mins	105 mins	120 mins	150 mins
Tetralin (blank)	0.5	0.7	0.9	1.0	1.2	1.4	1.6
+ 0.375 mls. Cobalt Naphthenate	12.6	-	14.2	-	12.7	-	10.0
+ 0.75 mls. Cobalt Naphthenate	29.4	30.3	34.7	36.1	31.4	30.4	-

Percentage of Oxygen Absorbed Present as Hydroperoxide.
(0.75 mls. Cobalt Naphthenate)

Weight of sample	1.7879 gms.
Titration (mls. $\frac{N}{10}$ Sodium Thiosulphate)	7.05

Total Hydroperoxide present $= \frac{28.2388}{1.7879} \times 7.05 \times 0.0082$

$= 0.9128$ gms.

Total oxygen absorbed at N.T.P.	= 259 mls.
Oxygen absorbed expressed as hydroperoxide	= 1.895 gms.
Oxygen absorbed present as hydroperoxide	= 48.2%

From these results it was apparent that metal catalysts of the oxidation reaction were also efficient catalysts for the decomposition of the hydroperoxide as was reflected in the low yields of hydroperoxide obtained with high catalyst concentrations (Figure XXVII). This fact explains the results obtained by Plissof(86) who experienced difficulty in the preparation of peroxides in the presence of metal oxidation catalysts. A close relation between these dual functions of the catalyst seemed highly probable, and it was decided to investigate the effect of cobalt naphthenate on the rate of the decomposition of the hydroperoxide.

The Decomposition of Tetralin Hydroperoxide in the Presence of Cobalt Naphthenate.

When solutions of cobalt naphthenate were added to a solution of the hydroperoxide in tetralin they were decolourised and, if the concentration of the hydroperoxide was sufficiently high, the reaction became violent and appreciable quantities of heat were evolved. Preliminary experiments demonstrated that the rate of the catalysed decomposition was too rapid for accurate measurement at 76°C. and the investigation was, therefore, carried out at 20°C.

The apparatus was of similar type to that used in the investigation of the kinetics of the thermal decomposition described in Section V. On transferring the samples for analysis to flasks, the latter were immediately placed in ice and an excess of potassium iodide added to prevent further decomposition of the hydroperoxide taking place. The results obtained are shown in Table XXVIII and illustrated in

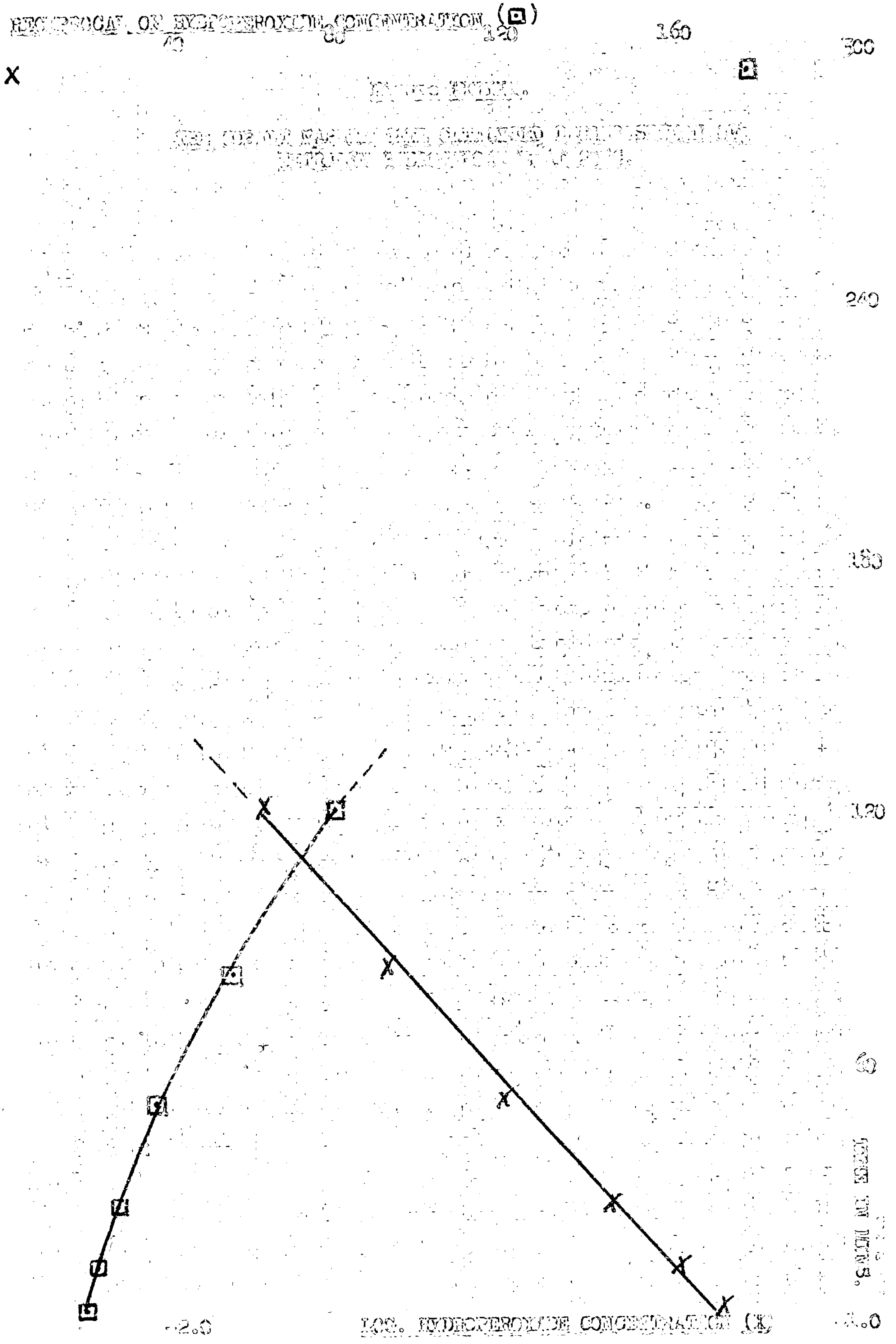

RECIPROCAL OF HYDROPEROXIDE CONCENTRATION (▣)
40
80
120
160
X
▣
300
240
180
120
60
TIME IN MINS.
-2.0
LOG. HYDROPEROXIDE CONCENTRATION (X)
-1.0

Figure XXVIII. The plot of the logarithm of the residual peroxide concentration against time was linear, and the decomposition was thus of the first order. Divergence from this first order relationship was noticeable in the later stages of the decomposition when the reaction rate showed signs of decreasing. This was also observed by George and Robertson(58) and is presumably a result of the destruction of catalyst during the course of the reaction.

The Effect of the Variation of the Catalyst Concentration.

The decomposition of the hydroperoxide by the addition of varying quantities of cobalt naphthenate solution was carried out under conditions identical to those described above. Results are shown in Table XXVIII and Figure XXIX.

Table XXVIII.

Decomposition of Tetralin Hydroperoxide in the Presence of Cobalt Naphthenate.

Time from Start of Decomposition in Minutes	Hydroperoxide per ml. Solution	Log. Hydroperoxide Concentration	Reciprocal of Hydroperoxide Concentration
2 mls Cobalt Naphthenate			
-	0.0640	-1.1941	15.63
10	0.0544	-1.2648	18.40
25	0.0426	-1.3702	23.45
50	0.0291	-1.5354	34.31
80	0.0196	-1.7081	51.06
120	0.0071	-1.8821	76.20
295	0.0056	-2.2500	177.80

(Cont'd)

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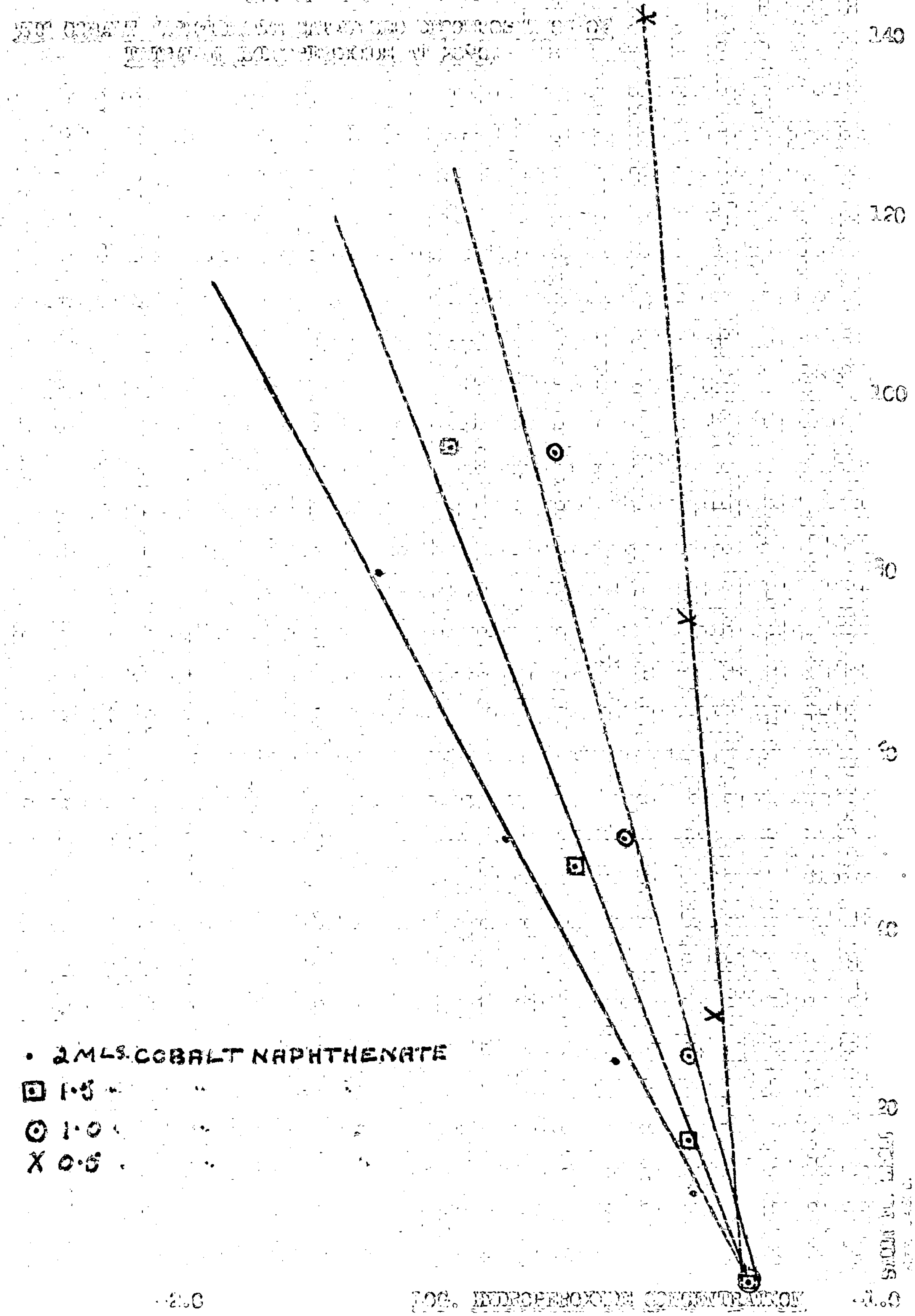


140
120
100
80
60
40
20
TIME IN MINS.
-2.0
LOG. HYDROPEROXIDE CONCENTRATION
-1.0
• 2 MLS. COBALT NAPHTHENATE
⊡ 1·5 " "
⊙ 1·0 " "
X 0·5 " "

Fig. XX.

VARIATION OF THE RATE OF DECOMPOSITION OF TETRALIN HYDROPEROXIDE WITH CATALYST CONCENTRATION

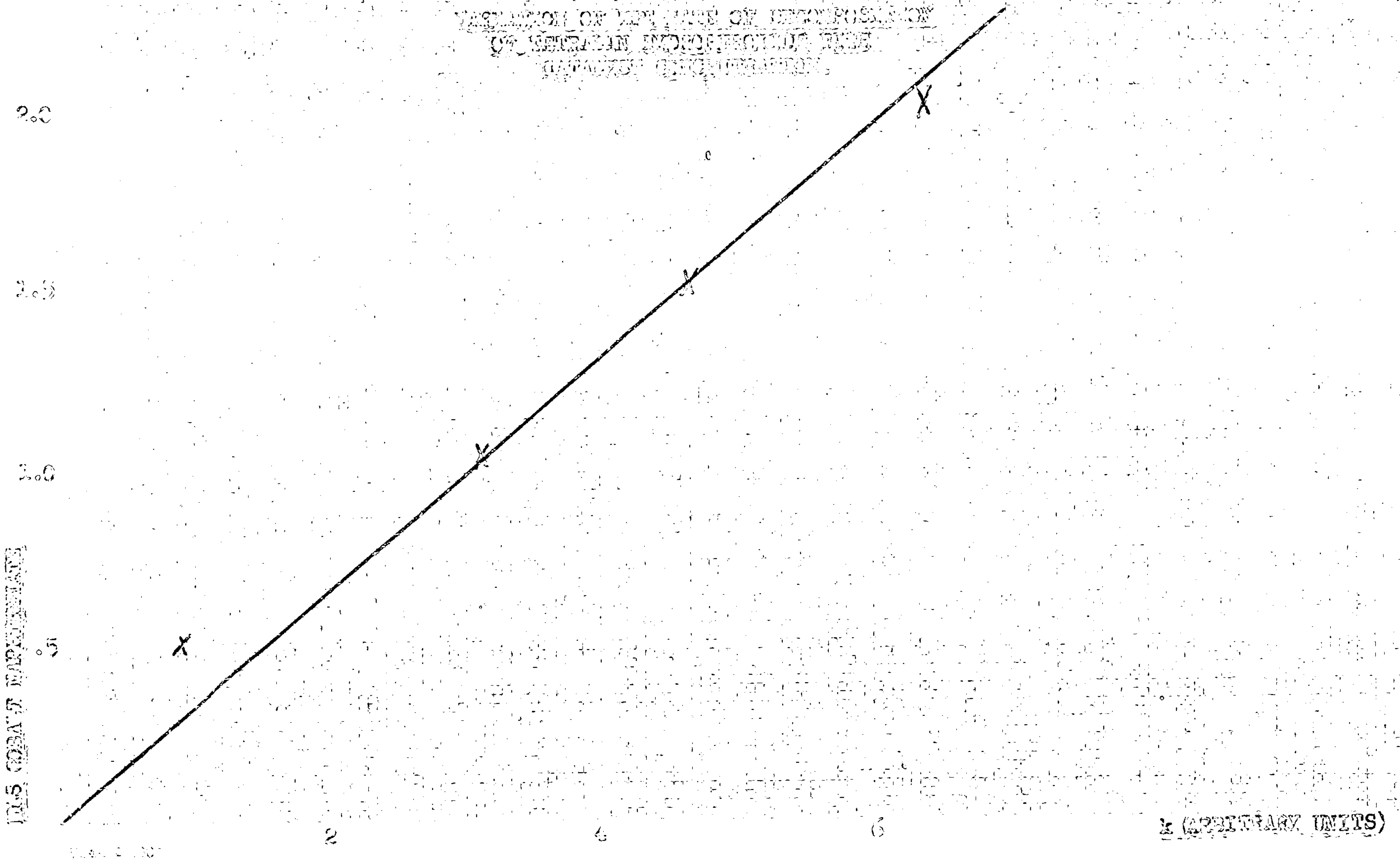


Table XXVIII. (Cont'd)

Decomposition of Tetralin Hydroperoxide in the Presence of Cobalt Naphthenate.

Time from Start of Decomposition in minutes	Hydroperoxide/gm. Solution	Log. Hydroperoxide Concentration
1.5 mls Cobalt Naphthenate		
-	0.0640	-1.1941
16	0.0536	-1.2708
47	0.0375	-1.4261
94	0.0253	-1.5968
1 ml. Cobalt Naphthenate		
-	0.0648	-1.1886
25	0.0571	-1.2733
50	0.0474	-1.3538
93	0.0391	-1.4378
0.5 ml. Cobalt Naphthenate		
-	0.0625	-1.2042
30	0.0595	-1.2258
75	0.0552	-1.2580
142	0.0497	-1.3037

Reaction velocities calculated from the slopes of the lines in Figure XXIX were plotted against the quantity of catalyst added (Figure XXX). The relationship was linear and the rate of the decomposition of the hydroperoxide was thus of the first order and was directly proportional to the concentration of the catalyst added. The latter relationship was derived from theoretical considerations by George, Rideal and Robertson(13)

Quantitative Examination of the Products of the Metal Catalysed Decomposition of Tetralin Hydroperoxide.

It has been assumed by most workers that the metal catalysed decomposition of hydroperoxides yields ketones in almost quantitative yield. Evidence is available, however, to the contrary, for example French Patent No. 37,351 covers the preparation of both α tetralol and α tetralone by the metal catalysed oxidation of tetralin, and a quantitative examination of the decomposition products of the hydroperoxide was therefore made.

Method.

Analytical methods were identical to those employed for the thermal decomposition, although recourse to the potentiometric method was found essential in most cases because of the difficulty in end point determination.

A solution of 0.5 gm. tetralin hydroperoxide in 5 mls. tetralin was decomposed at 76°C. in an atmosphere of nitrogen by the addition of 4 mls. of cobalt naphthenate solution, and analysis was carried out as previously described. Results obtained are shown in Table XXIX.

Table XXIX.

The Decomposition of Tetralin Hydroperoxide in the Presence of Cobalt Naphthenate.

	Molar %
Ketone as α Tetralone	48.0
Alcohol as α Tetralol	33.0
Acid (as mono-basic)	2.0
Saponifiable material	1.0
Oxygen	16.1

The addition of an increased quantity of catalyst had no significant effect on the relative quantities of the products of decomposition, although some interaction of the acid liberated during oximation with the excess cobalt present seemed apparent because the solution turned pale green in colour during the ketone determination and probably resulted in the analytical result being slightly low.

Table XXX.

The Decomposition of Tetralin Hydroperoxide in the Presence of an Increased Concentration of Cobalt Naphthenate (8 mls.)

Ketone as α Tetralone	46.0%
Alcohol as α Tetralol	30.0%

It can be seen from Tables XXIX and XXX that the products of the catalysed decomposition of the hydroperoxide differed little from those of the thermal decomposition, and it seemed probable that the catalysed decomposition also involved the production of the hydroxyl radical. Repetitions were therefore made of the glycol splitting experiments (Section V) using the low temperature catalysed decomposition of the hydroperoxide as a possible source of hydroxyl radicals.

Evidence of the Presence of Free Radicals during the Catalysed Decomposition of Tetralin Hydroperoxide.

Glycol Splitting.

Ethylene Glycol.

Five gms. of the hydroperoxide in 20 mls. ethylene glycol were decomposed by the addition of an excess of cobalt naphthenate. The gaseous products were blown by a stream of nitrogen into a solution of dimedone in dilute alcohol. After refluxing on a water bath a dimedone derivative was formed which, after recrystallisation from dilute alcohol, melted at 189°C. and gave no depression with an authentic sample of the dimedone derivative of formaldehyde.

Pinacol.

Five gms. of the hydroperoxide and two gms. of pinacol were dissolved in 20 mls. of glacial acetic acid. Decomposition was effected by the addition of excess cobalt naphthenate and the gaseous products blown into a solution of 2:4-dinitrophenyl hydrazine in dilute hydrochloric acid. A dinitrophenyl hydrazone was obtained which, after recrystallisation from alcohol, melted at 126°C. and gave no depression with an authentic sample of the dinitrophenyl hydrazone of acetone.

2:3-Butylene Glycol.

Five gms. of the hydroperoxide in 20 mls. of 2:3-butylene glycol were decomposed by the addition of excess cobalt naphthenate solution. The gaseous products were blown into a dilute alcoholic solution of dimedone. After refluxing with a little acetic acid a dimedone anhydride was formed which, after recrystallisation from dilute alcohol, melted at 175°C. and gave no depression with an authentic sample of the dimedone anhydride of acetaldehyde.

Glycerol.

Five gms. of the hydroperoxide in 20 mls. of glycerol were decomposed by the addition of an excess of cobalt naphthenate. The gaseous products of the decomposition were blown into a solution of 2:4-dinitrophenyl hydrazine in dilute hydrochloric acid. A dinitrophenyl hydrazone was obtained which, after recrystallisation from alcohol, melted at 165°C. and gave no depression with an authentic sample of the diphenyl hydrazone of formaldehyde.

Hydroxylated Products of the Metal Catalysed Decomposition of Tetralin Hydroperoxide.

Methods identical to those employed in Section VI for the thermal oxidation gave samples of α tetralol (phenyl urethane, M.P. 122°C.) and o.phenol butyric acid (M.P. 68°C.). The mode of formation of the latter and its implications regarding the participation of the hydroxyl radical in the reaction have been discussed in Section V.

Discussion.

Possible alternatives for the mechanism of the catalysis of the oxidation of hydrocarbons by metal salts are:-

(1) Activation of the oxygen molecule, which can then react with the hydrocarbon to form the tetralyl radical:-

$$M^{++} \longrightarrow M^{+++} + \mathcal{E}$$

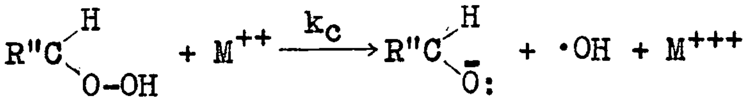
$$\mathcal{E} + O_2 \longrightarrow (\cdot O\text{-}O:)^{-} + H^{+} \rightleftharpoons \cdot O\text{-}O\text{-}H$$

$$\cdot O\text{-}O\text{-}H + R''CH_2 \longrightarrow HO\text{-}OH + R''\underset{\bullet}{C}{}^{/H}$$

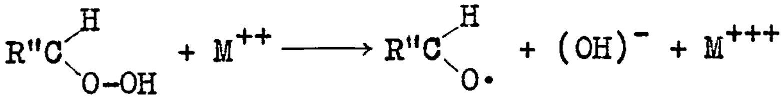
(2) The production of chain initiators by the catalysed decomposition of the hydroperoxide.

Baxendale, Evans and Park(169) have observed that during the polymerisation of olefines with metallic salt catalysts, such as Fe^{++}, oxygen was absorbed by the olefine only when the polymerisation was proceeding. This observation indicates that metallic salt catalysts do not function by activation of oxygen, but that hydrocarbon radical formation must occur before oxygen is absorbed. Mechanism (2) is also favoured by the observation that the rate of oxygen uptake increases after oxygen absorption has proceeded for some time (compare Table XXVII).

Hydroxyl or alcohol radicals may be produced during the catalysed decomposition of the hydroperoxide by the following reactions:-

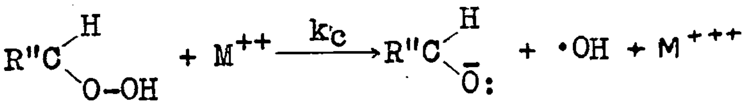


$$R''C\begin{array}{l}H\\O\text{-}OH\end{array} + M^{++} \xrightarrow{k_c} R''C\begin{array}{l}H\\\bar{O}:\end{array} + \cdot OH + M^{+++} \qquad (3)$$



$$R''C\begin{array}{l}H\\O\text{-}OH\end{array} + M^{++} \longrightarrow R''C\begin{array}{l}H\\O\cdot\end{array} + (OH)^{-} + M^{+++} \qquad (4)$$

The decomposition of tetralin hydroperoxide is catalysed by the same metallic cations which catalyse the decomposition of hydrogen peroxide(37)(88), and this similarity suggests that hydroxyl radicals are also produced in the former case. The evidence obtained from the glycol splitting experiments and the nature of the hydroxylated products of catalysed oxidations confirms the production of hydroxyl radicals during the decomposition. The choice of reaction (3) is also favoured by the fact that the production of hydroxyl radicals, which can function as chain initiators (Section VII), would accord with the observation that electron donating catalysts can both decompose the hydroperoxide and accelerate the oxidation process. This dual function can be clearly seen from the following reaction sequence:-



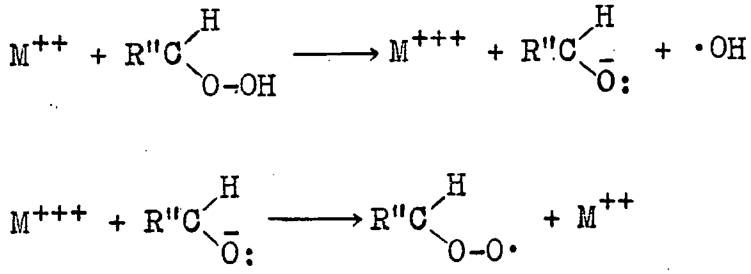
$$R''C\begin{array}{l}H\\O\text{-}OH\end{array} + M^{++} \xrightarrow{k_c} R''C\begin{array}{l}H\\\bar{O}:\end{array} + \cdot OH + M^{+++}$$

$$T + \cdot OH \longrightarrow R_1 + H_2O$$

$$R_1 + O_2 \longrightarrow R_2$$

$$R_2 + T \longrightarrow P + R_1$$

Thus, the greater the concentration of M^{++} the higher the rate of decomposition of the peroxide and the greater the rate of chain initiation. The catalytic power of the metallic salt is not completely destroyed by the initial electron transfer, for Weiss(191) has shown that peroxides, when reacting with metallic ions, may act both as donators and acceptors of electrons:-



$$M^{++} + R''C\overset{H}{\underset{O-OH}{}} \longrightarrow M^{+++} + R''C\overset{H}{\underset{\bar{O}:}{}} + \cdot OH$$

$$M^{+++} + R''C\overset{H}{\underset{\bar{O}:}{}} \longrightarrow R''C\overset{H}{\underset{O-O\cdot}{}} + M^{++}$$

The steady reaction state will thus be dependent upon the equilibrium between the oxidised and reduced states of the metallic cation.

The rate of oxidation reactions at high catalyst concentration has been shown(72)(73) to be independent of the catalyst concentration. George, Rideal and Robertson(13) explained this observation by postulating that the metal catalyst could both initiate and terminate reaction chains. This type of chain initiation and termination was suggested by Haber and Weiss(88) for the metal catalysed decomposition of hydrogen peroxide, thus:-

Initiation

$$Fe^{++} + HO\text{-}OH \longrightarrow Fe^{+++} + \cdot OH + (OH)^{-}$$

Termination

$$Fe^{++} + \cdot OH \longrightarrow Fe^{+++} + (OH)^{-}$$

BIBLIOGRAPHY.

(1) Bone and Wheeler, J.C.S. 1088, 1903.

(2) Waters, The Chemistry of Free Radicals, Oxford University Press, 232, 1946.

(3) Schonbein, J. Prakt. Chem. 93, 24, 1862.

(4) Clausius, Pogg, Ann. 103, 644, 1858.

(5) Van't Hoff, Zt. Phys. Chem. 16, 411, 1895.

(6) Hoppe-Seyler, Zt. Physiol. Chem. 2, 22, 1878.

(7) Bach, Compt. Rendu Acad. Sci. 124, 951, 1897.

(8) Engler and Wild, Berichte, 30, 1669, 1897.

(9) Armstrong (see reference 10)

(10) Bone, J.C.S. 1599, 1933.

(11) Stephens, J.A.C.S. 50, 2523, 1928.

(12) Farmer and Sundralingham, J.C.S. 121, 1942.

(13) George, Rideal and Robertson, Proc. Roy. Soc. 185A, 288, 1946.

(14) Egerton, Smith and Ubbelohde, Phil. Trans. Roy. Soc. 234, 433, 1935.

(15) Callendar, Engineering, 123, 147, 1927.

(16) Egerton, Nature, 121, 10, 1928.

(17) Ubbelohde, Proc. Roy. Soc. 152A, 354, 1935.

(18) Ivanov, Acta Physicochimica U.R.S.S., 9, 421, 1938.

(19) Mardles, J.C.S. 872, 1928.

(20) Rieche, Alkyl Peroxyde und Ozonide, Steinkopf, Dresden, 1931.

(21) Hock and Susemihl, Berichte, 66, 61, 1933.

(22) Hock and Gänicke, Berichte, 71, 1430, 1938.

(71) Bloomfield and Farmer, J. Soc. Chem. Ind. 54, 125T, 1935.

(72) Cook, J.C.S. 1768, 1938.

(73) Davis, Lincoln, Byrkit and Jones, Ind. Eng. Chem. 33, 339, 1941.

(74) Robinson, Biochem. J. 18, 255, 1924.

(75) Annual Report of the Mines Department of W.Australia,1935.

(76) Berl and Winnacker, Zt. Phys. Chem. 148, 261, 1930.

(77) Wieland, Annalen, 464, 101, 1928.

(78) Wieland, Annalen, 475, 1, 1929.

(79) Willstätter and Sonnenfeld, Berichte, 46, 2952, 1913.

(80) Criegee, Annalen, 522, 75, 1936.

(81) Manchot, Zt.Anorg. Chem. 211, 1, 1933.

(82) Hale, J. Phys. Chem. 33, 1633, 1929.

(83) Wieland and Richter, Annalen, 486, 226, 1931.

(84) Waters, The Chemistry of Free Radicals, O.U.P. 233, 1946.

(85) Ivanov, Savinova and Mikhailova, Compt. Rendu de l'Acad. Sci. U.R.S.S. 25, 34, 1939.

(86) Plissoff,Bull. Soc. Chim. Paris, 3(5), 425, 1274, 1281.

(87) Haber and Willstätter, Berichte, 64, 2844, 1931.

(88) Haber and Weiss, Proc. Roy. Soc. 147A, 333, 1934.

(89) Bamberger and Kitschelt, Berichte, 23, 1561, 1890.

(90) Schroter, Zt. fur Physiol. Chem. 106, 266, 1913.

(91) Strauss and Lemmel, Berichte, 54, 29, 1921.

(92) Hartmann and Seiberth, Helv. Chim. Acta 15, 1390, 1932.

(93) Medvedev and Podyapolskaya, J. Phys. Chem. U.R.S.S. 25, 34, 1939.

(94) Bodenstein, S.B. preuss. Akad. Wiss. 73, 1931.

(95) George and Robertson, Proc. Roy. Soc. 185A, 309, 1946.

(96) Alyea and Backstrom, J.A.C.S. 51, 90, 1929.

(97) Evans, J. Inst. Pet. Tech. 24, 537, 1938.

(98) Nussle, Perkins and Toennies, Am. J. Pharm. 107, 29, 1935.

(99) Engler and Weissberg, Kritische Studien über die Vorgänge der Autoxydation, 1903.

(100) Stephens, J.A.C.S. 50, 568, 1928.

(101) Yule and Wilson, Ind. Eng. Chem. 23, 1254, 1931.

(102) Klason, Chem. Ztg., 35, 537, 1911.

(103) Wheeler, Oil and Soap, 9, 989, 1932.

(104) Lee, Dept. Sci. Ind. Research Report, Food Invest. Board, 1929-30.

(105) Hyman and Wagner, J.A.C.S. 52, 4345, 1930.

(106) French, Ind. Eng. Chem. 27, 724, 1935.

(107) Marks and Morrell, Analyst, 54, 504, 1929.

(108) Sharkey, J.A.C.S. 62, 190, 1940.

(109) Risbey and Nisbet, Analyst, 70, 827, 1945.

(110) Larsen, Thorpe and Armfield, Ind. Eng. Chem. 34, 282, 1942.

(111) Balsbaugh and Oncley, Ind. Eng. Chem. 31, 318, 1939.

(112) Stephens, J.A.C.S. 58, 219, 1936.

(113) Henderson and Young, J. Phys. Chem. 46, 670, 1942.

(114) Almquist and Branch, J.A.C.S. 54, 2293, 1932.

(115) Bolland, Proc. Roy. Soc. 186A, 218, 1946.

(116) Yamada, J. Soc. Chem. Ind. Japan, 39, Suppl. binding, 450-2, 1936.

(117) Semenoff, Chem. Kinetics and Chain Reactions, O.U.P. 1935.
(a) Page 358
(b) " 68
(c) Chapter 12.

(118) Milas, J.A.C.S. 52, 739, 1930.

(119) French, Olcott and Mattill, Ind. Eng. Chem. 27, 724, 1935

(120) Wagner and Brier, Ind. Eng. Chem. 23, 40, 1931.

(121) George, Proc. Roy. Soc. 185A, 337, 1946.

(122) Hey and Waters, Chemical Reviews, 21, 169, 1937.

(123) Reynhart, Rec. Trav. Chim. Pays-Bas. 46, 62, 1927.

(124) McClure, Robertson and Cuthbertson, Can. J. Res. 20B, 103, 1942.

(125) Grieve and Hey, J.C.S. 1797, 1934.

(126) Waters, J.C.S. 113, 1937.

(127) Fieser, Clapp and Daudt, J.A.C.S. 64, 2052, 1942.

(128) Waters, J.C.S. 2007, 1937.

(129) Makin and Waters, J.C.S. 843, 1938.

(130) Kharasch, Mayo and Goldberg, J.A.C.S. 60, 2063, 1938.

(131) Gilman and Wood, J.A.C.S. 48, 806, 1926.

(132) Waters, J.C.S. 153, 1942.

(133) Rust and Vaughan, J. Org. Chem. 7, 491, 1942.

(134) Ziegler, Annalen, 551, 80, 1942.

(135) Whitmore and Pedlow, J.A.C.S. 63, 785, 1941.

(136) Waters, Trans. Farad. Soc. 42, 184, 1946.

(137) Huebner, Ames and Bubl, J.A.C.S. 68, 1621, 1946.

(138) Sequin, Compt. Rendu, 216, 667, 1943.

(139) Criegee, Berichte, 69, 2758, 1936.

(140) Arnold and Collings, J.A.C.S. 61, 1407, 1939.

(141) Ritter and Sharpe, J.A.C.S. 59, 2531, 1937.

(142) Denison and Condit, Ind. Eng. Chem. 37, 1103, 1945.

(143) Haworth, Heilbron and Hey, J.C.S. 372, 1940.

(144) Kynch and Penney, Proc. Roy. Soc. 179A, 214, 1942.

(145) Baughan, Evans and Polanyi, Trans. Farad. Soc. 37, 377, 1944.

(146) Bolland and Gee, Trans. Farad. Soc. 42, 244, 1946.

(147) Pauling, The Nature of the Chemical Bond, Cornell, 1939.

(148) George and Robertson, J. Inst. Pet. 32, 400, 1946.

(149) Bowen, Chemical Aspects of Light, O.U.P., 137, 1942.

(150) Bockemüller and Pfeuffer, Annalin, 537, 178, 1939.

(151) Brown and Daniels, J.A.C.S. 62, 2820, 1940.

(152) Waters, The Chemistry of Free Radicals, O.U.P. 178, 1946.

(153) U.S.P. 2,369,181.

(154) Weiss, Trans. Farad. Soc. 42, 116, 133, 1946.

(155) Nozaki and Bartlett, J.A.C.S. 68, 1686, 1946.

(156) Bartlett and Altschul, J.A.C.S. 67, 816, 1945.

(157) Franck and Rabinowitch, Trans. Farad. Soc. 30, 120, 1934.

(158) Kipping and Hill, J.C.S. 144, 1899.

(159) Bell, J.C.S. 2903, 1932.

(160) Van Nieuwenberg, Micro. Chimica Acta, 1, 71, 1937.

(161) Tchoubar, Compt. Rendu, 214, 117, 1942.

(162) U.S.P. 2,298,405.

(163) Stern and Polak, Acta Physicochimica U.R.S.S. 11, 797, 1939.

(164) German Patent 651,771.

(165) Blomquist, Johnson and Sykes, J.A.C.S. 65, 2446, 1943.

(166) Medvedev, Koritzkaya and Alexeyeva, J. Phys. Chem. U.R.S.S. 17, 391, 1943.

(167) Medvedev, Chilikina and Klimenkoo, Acta Physicochimica U.R.S.S. 11, 751, 1939.

(168) Waters, Nature, 158, 380, 1946.

(169) Baxendale, Evans and Park, Trans. Farad. Soc. 42, 155, 1946.

(170) Dwyer and Oldenberg, J. Chem. Phys. 12, 351, 1944.

(171) Cross and Bevan, J.C.S. 748, 1899.

(172) Cross, Bevan and Heiberg, Berichte, 33, 2015, 1900.

(173) Oyamada, J. Soc. Chem. Ind. Japan, 41, 209B, 1938.

(174) Martinon, Bull. Soc. Chim. 43, 156, 1885(ii).

(175) Dakin, J. Biol. Chem. 4, 65, 227, 1908.

(176) Milas, J.A.C.S. 59, 2342, 1937, ibid, 58, 1302, 1936.

(177) Egloff, The Reactions of Pure Hydrocarbons, Reinhold, 687, 1937.

(178) German Patent 709,322.

(179) Strauss and Lemmel, Berichte, 46, 232, 1913.

(180) Jenkins, J.A.C.S. 57, 2733, 1935.

(181) Paquot, Bull. Soc. Chim. 12, 450, 1945.

(182) Riley, Morley and Friend, J.C.S. 1879, 1932.

(183) Wallach, Annalen, 437, 148, 1924.

(184) Rauh, Smith, Banks and Diehl, J. Org. Chem. 10, 199, 1945.

(185) Strauss, Bernoully and Mautner, Annalen, 444, 165, 1925.

(186) Bamberger and Lodter, Berichte, 23, 1890, 197.

(187) Hey, Chem. Soc. discussion, London, 21.11.46.

(188) Kharasch and Mayo, J. Org. Chem. 2, 76, 1937.

(189) Karrer and Schmid, Helv. Chim. Acta, 29, 523, 1946.

(190) Tobias, Farben. Ztg. 45, 68, 1940.

(191) Weiss, Trans. Farad. Soc. 31, 1547, 1935 and J. Phys. Chem. 41, 1107, 1937.

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