OXIDATION OF PARA-CYMENE

LIQUID-PHASE CATALYTIC OXIDATION
OF
PARA-CYMENE

By

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SCOPE AND CONTENTS: A study has been made of the liquid-phase oxidation of p-cymene with air in the presence of cobalt naphthenate at temperatures 50, 105, and 160 °C. A solid carboxylic acid product has been isolated and a chromatographic procedure developed for its quantitative separation into the following compounds: cumic acid, p-acetylbenzoic acid, p-(α-hydroxyisopropyl)benzoic acid, and p-(α-hydroperoxyisopropyl)benzoic acid. The hitherto unreported hydroperoxy-acid has been characterized by (a) neutralization equivalent, (b) peroxidic oxygen content, (c) reduction to the above mentioned hydroxy-acid, and (d) metal-catalyzed decomposition to the hydroxy- and keto-acids. Two previously reported products of cymene oxidation, p-toluic acid and terephthalic acid, were not produced in the present study. Large amounts of tarry products were formed at the higher temperatures, and lower yields of the carboxylic acids were obtained.

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INTRODUCTION

During the last fifteen years the oxidation of hydrocarbons has received a great deal of attention from both the theoretical and practical points of view. A consideration of the oxidation of p-cymene with molecular oxygen at moderate temperatures (autoxidation) offers many complexities. The following points should be borne in mind:

(a) p-Cymene is a hydrocarbon, and a very large volume of published work is available on the autoxidation of hydrocarbons in general (1, 2, 3, 4, 5, 6, 7, 8, 9).

(b) It is further a member of a sub-family of hydrocarbons, i.e., alkylbenzenes (10, 11, 12, 13, 14, 15, 16, 17, 18) on which a great deal more specialized work has been reported, for example, tetralin (19, 20, 21, 22, 23, 24, 25, 26, 27, 28) and ethylbenzene (11, 14, 29, 30, 31, 32, 33, 34, 35).

(c) It is one of a number of alkylbenzenes in which the main point of oxidative attack is a tertiary carbon atom (36, 37), for example, cumene (12, 14, 32, 33, 34, 38, 39, 40, 41, 42, 43, 44, 45) and triarylmethanes (46).

(d) p-Cymene (p-$CH_3C_6H_4CH(CH_3)_2$) has two points of oxidative attack, and has been reported to yield products resulting from attack on one group while the other remains unchanged, and other products resulting from attack on both the isopropyl group and the methyl group. Thus, Palmer and Bibb (47, 48) have patented processes for producing cumic acid (p-HOOC.$C_6H_4CH(CH_3)_2$), dimethyl-p-tolylcarbinol (p-$CH_3C_6H_4COH(CH_3)_2$), and p-methylacetophenone (p-$CH_3C_6H_4COCH_3$) in the same reaction mixture by the air oxidation of p-cymene at 30° C.

Theoretical aspects of the autoxidation of tetralin have been studied exhaustively and of ethylbenzene to a somewhat lesser degree. Cumene has received a considerable amount of attention in recent literature, since it is now made synthetically in large quantities, but p-cymene, a natural product, has been much less thoroughly studied. Several patents, however, have been issued covering conversion of both cumene and cymene to useful oxidation products.

An investigation of the autoxidation of p-cymene, therefore, has been initiated in an attempt to extend our knowledge of the mode of oxidative attack on alkylbenzenes at a tertiary carbon, and, in addition, to point up any unique features in the oxidation of this hydrocarbon with two side chains, as compared to cumene with one.

A second aim of the investigation was to determine optimum conditions for the oxidation of p-cymene to terephthalic acid (p-$C_6H_4(COOH)_2$). The industrial importance of terephthalic acid has lately increased to a marked extent due to the development of polyester-type fibers. "Dacron", made by Dupont in the United States, and "Terylene", made by Imperial Chemical Industries in Britain, are examples. The preparation of terephthalic acid by liquid-phase oxidation of other compounds has been reported in the patent literature. A Dupont patent (49) reports the production of terephthalic acid by liquid-phase oxidation of p-toluic acid in acetic acid solution with a lead acetate catalyst at elevated temperatures and pressures. A British patent (50) has claimed p-xylene as the starting material for an autoxidation reaction utilizing cobalt naphthenate as catalyst.

With these two objectives in mind, the experimental program was designed to approach both goals simultaneously. From the reaction products of p-cymene autoxidations the acidic products were separated from other compounds including unreacted hydrocarbon, and all efforts were directed to separating the acids one from another, and to identifying each. While we were searching for terephthalic acid we were also investigating a group of reaction products very important to a study of p-cymene oxidation mechanisms.

In addition to the objectives as stated, however, another influence tended to direct the work firstly to an investigation of the acidic oxidation products , namely, an apparent conflict in the literature concerning the nature of the acids formed. Senseman and Stubbs (51) studied the oxidation of p-cymene at 140-160° C. in the presence of manganese dioxide. The chief products reported were p-toluic acid and p-methylacetophenone. In addition, some formaldehyde, formic acid, and terephthalic acid (under prolonged oxidation) were obtained, as well as carbon dioxide and water.

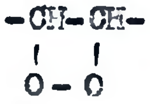
On the other hand, Palmer and Bibb (47, 48) patented processes involving oxidation of p-cymene at 35-50° C. in the presence of special catalysts and the products reported were cumic acid (40 per cent yield on converted hydrocarbon) p-methylacetophenone, and dimethyl-p-tolylcarbinol. In a Swedish patent (52) also, cumic acid and dimethyl-p-tolylcarbinol are listed as major products of p-cymene oxidation. The catalyst was cobalt or manganese cuminate or finely divided potassium permanganate, and the recommended reaction temperature 60-125° C. Shrader (53) heated p-cymene with air under pressure at 210° C. in the presence of sodium carbonate solution, and obtained cumic acid, p-toluic acid, and terephthalic acid, with small amounts of formic, acetic, and oxalic acids. It is seen that cumic acid was not isolated by Senseman and Stubbs, even as a minor product, whereas p-toluic acid was not reported in any of the recent patents. Furthermore, the desired acid, terephthalic, has never been a major product of p-cymene autoxidation.

In the present work, an acid fraction was isolated from each oxidation mixture and a partition chromatographic method was developed for quantitatively separating the component acids. The isolated compounds, all solids, were characterized. Unfortunately, however, terephthalic acid was not among them. The complexities of this problem were such that time did not permit a study of the other oxidation products. It was possible only to study the effect of reaction temperature on the composition of the acidic product from the oxidation of p-cymene in the presence of cobalt naphthenate catalyst.

In addition to the work in the laboratory, it was necessary to conduct an extensive literature survey into hydrocarbon autoxidation, dwelling particularly upon the oxidation of alkylbenzenes. No adequate review of this important and rapidly expanding subject was available . A rather lengthy HISTORICAL INTRODUCTION is the result.

HISTORICAL INTRODUCTION

The overall process of hydrocarbon autoxidation in the liquid phase consists of two distinct reaction sequences, namely, the formation and the decomposition of an intermediate that is peroxidic in character. Early studies in olefin oxidation led to a theory that molecular oxygen adds to the double bond forming a cyclic product (I). It has been superseded by the view that the peroxidic intermediate is a <u>hydroperoxide</u> in which the unsaturation of the olefin is preserved (II). Thus, for example, Criegee, Pilz, and Flygare (54) have shown the peroxide of cyclohexene to have structure (III).



$$\begin{array}{c}-CH-CH-\\ |\quad\ |\\ O-O\end{array}$$

(I)

$R\text{-}OOH$ (II)

(III)

The course of the reaction for saturated as well as for unsaturated hydrocarbons is now considered to proceed through the hydroperoxide stage. In fact, stable hydroperoxides have been isolated from the products of autoxidation of many hydrocarbons including olefins, alkylbenzenes, and paraffins, for example, cyclohexene (14, 54, 55), tetralin (22, 24, 27), triarylmethanes (46), ethylbenzene (11), p-xylene (11), cumene (12, 38), diphenylmethane (12), indane (56), and octahydroanthracene (57).

For the autoxidation of any hydrocarbon, then, the overall reaction can be represented thus:

$$\mathrm{RH} \xrightarrow{\text{STEP 1}} \mathrm{ROOH} \xrightarrow{\text{STEP 1}} \text{PRODUCTS}$$

The formation of a hydroperoxide, step 1, is generally conceded to proceed by one path, a free radical chain mechanism. However, the decomposition, or step 2, has been shown to proceed by more than one path. Products formed depend on whether the decomposition is caused by acids, by bases, or by breakdown into free radicals.

Kharasch and coworkers have approached the problem of autoxidation by studying the chemistry of peroxides and hydroperoxides. Their series of papers entitled "The Chemistry of Hydroperoxides" (40, 41, 58 to 67 inclusive) is recent and very comprehensive.

With this introduction, a detailed examination of the two steps of hydrocarbon oxidation can now be made. Kharasch's work is of prime importance since much of it deals with cumene hydroperoxide. Earlier research on tetralin and ethylbenzene is also pertinent.

Step 1 - Hydroperoxide Formation

The reaction of oxygen with a hydrocarbon is generally conceded to proceed by a free radical chain mechanism to form a hydroperoxide. Initiation may be induced by several means. Thus, Hock and his associates (11, 12, 24, 55, 56, 57, 68, 69) have studied the autoxidation of a variety of hydrocarbons under the activation of ultra-violet light. George and Robertson have investigated the thermal oxidation of tetralin (20), and the benzoyl peroxide-initiated oxidation (21), the surface-catalyzed oxidation (22), and the heavy metal-catalyzed oxidation (23) of the same hydrocarbon.

The general reaction sequence may be represented as follows (3):

Initiation $RH \xrightarrow{\text{(activation)}} R\cdot + H\cdot$ (i)

Propagation $R\cdot + O_2 \longrightarrow ROO\cdot$ (ii)

$ROO\cdot + RH \longrightarrow ROOH + R\cdot$ (iii)

Termination $R\cdot + R\cdot \longrightarrow RH + R(-H)$ (iv)

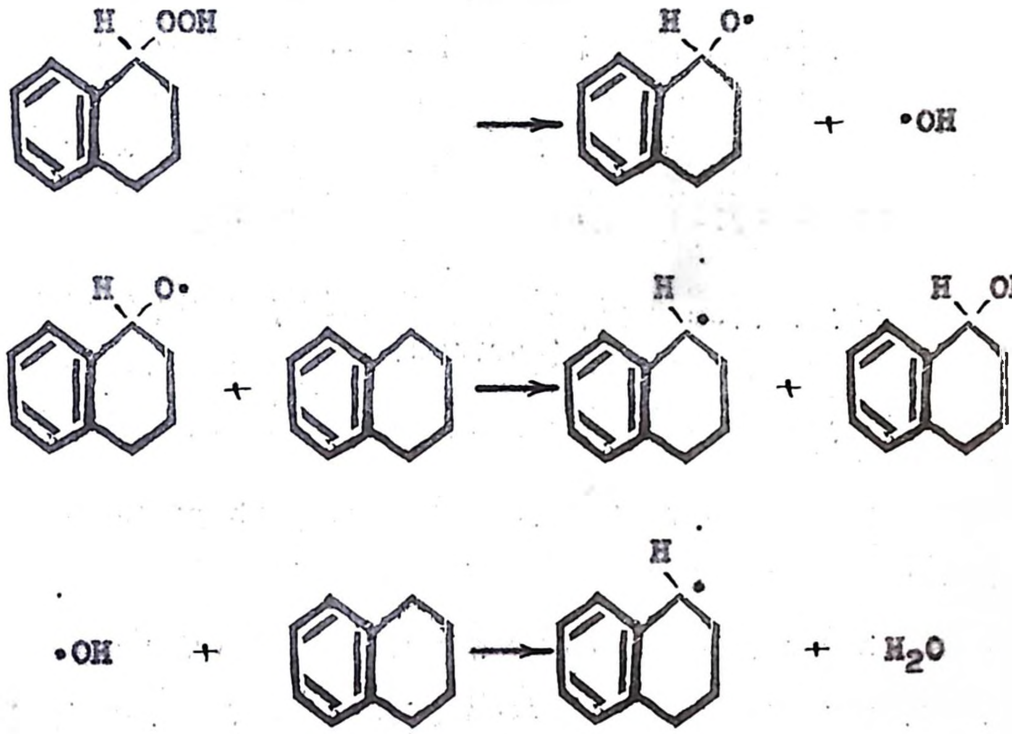
$ROO\cdot + \cdot OH \longrightarrow ROH + O_2$ (v)

$R\cdot + R\cdot \longrightarrow RR$ (vi)

etc.

Initiation

The free radical chain mechanism, represented by equations (ii) and (iii), obviously needs as a starting point an R• radical. Production of the radical, i.e., initiation of the chain, can be explained as follows using the autoxidation of tetralin as an example. Something, possibly light, heat, or an impurity in the hydrocarbon, causes an α-tetralyl radical to be produced. The chain reaction with oxygen proceeds, and many hydroperoxide molecules are produced for every chain. Some of these decompose to produce new radicals which are capable of initiating new chains.

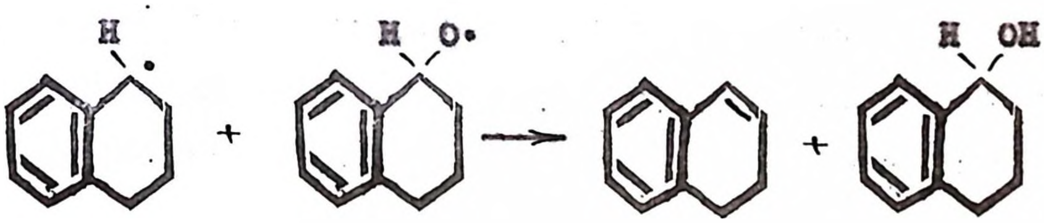


(vii)

(viii)

(ix)

α-Tetralol and water, shown in the equations, are both found in the products of oxidation, as is also 1,2-dihydronaphthalene (70).



(x)

This explanation is consistant not only with the products formed, but also with the autocatalytic nature of the reaction.

Robertson and Waters (25) report that the autoxidation of tetralin at 76° C., in the absence of a catalyst, passes through four distinct rate stages.

1. An initial period of some hours, during which a very minute amount of oxygen is absorbed, but the peroxide content of the liquid gradually increases.
2. An autocatalytic stage in which the reaction accelerates until the peroxide content is about 5 per cent.
3. A steady state, with constant and fairly rapid oxygen uptake, which persists until about 30 per cent of the tetralin has oxidized.
4. Finally, a decline in the rate of autoxidation when there still remains a considerable percentage of unreacted hydrocarbon.

Throughout stages 1 and 2, together termed the induction period, the hydroperoxide is formed quantitatively. In fact, at least 95 per cent of the absorbed oxygen is estimable as the hydroperoxide. Decomposition of hydroperoxide becomes apparent in stage 3, and, eventually in stage 4, there is more hydroperoxide decomposing than forming.

It has further been shown that tetralin hydroperoxide is definitely a catalyst for the autoxidation of tetralin.

By adding 5 per cent pure tetralin hydroperoxide to the tetralin before commencing an oxidation, the induction period is not observed. Similar results are found when benzoyl peroxide is added.

These observations are also easily explained. Tetralin hydroperoxide and benzoyl peroxide, ready sources of free radicals, cause many chains to start immediately, so that the uptake of oxygen is rapid from the beginning. No autocatalytic stage is observed.

More difficult to explain is the absence of an induction period in the metal-ion catalyzed autoxidation. Heavy metal catalysis in oxidation is a very complicated subject, and one of great importance. Some of the work which has appeared in the literature is of interest here.

George (23) noted that the oxidation rate for tetralin is independent of the catalyst concentration above a certain value. The author explained this phenomenon in terms of the following rate equation:

$$\text{Rate} = \frac{A + Dm}{B + Cm}$$

where m = catalyst concentration

A = number of chains started per unit time in the uncatalyzed reaction

D = number of chains started per catalyst molecule

$1/B$ = uncatalyzed chain length

$1/B + Cm$ = catalyzed chain length

The maximum rate is given when $Dm > A$ and $Cm > B$. This situation will occur if the catalytic formation of the hydroperoxide is a chain reaction in which the catalyst both starts and stops chains, and the catalytic initiation and termination rates are large compared with the thermal initiation and termination rates.

In connection with this theory, the catalysts in question were ferric and copper stearates and the hydrocarbon was tetralin. George, Rideal, and Robertson (5) reported similar results for copper stearate with ethylbenzene, and cobalt stearate with a long-chain hydrocarbon.

Another point of interest in connection with tetralin, pointed out by George (21), is that the kinetics of the heavy metal-catalyzed oxidation and the benzoyl peroxide initiated oxidation are completely similar. That is, oxidation rates are independent of catalyst concentration above a certain value. He suggests, then, that since a free radical mechanism is unquestionably operative in the presence of benzoyl peroxide, the same will hold true for the metal-ion catalyzed oxidation.

The actual detailed mechanisms involving such ions are not completely understood. George, Rideal, and Robertson (5) have postulated that the catalyst activates the oxygen. Later, Robertson and Waters (28) suggested that the catalyst causes decomposition into free radicals of the hydroperoxide, formed by thermal oxidation.

The latter view is supported by Bawn (71), who outlines recent work on the action of cobalt ions in the oxidation of both aldehydes and hydrocarbons. The onset of oxygen absorption was observed to correspond with a change in valency of the metal from cobaltous to cobaltic (pink to green). In the case of hydrocarbons this is attributed to the oxidizing action of hydroperoxide.

Bawn's general reaction scheme is as follows:

$$Co^{+2} + ROOH \longrightarrow Co^{+3} + RO\cdot + OH^{-} \text{ or } RO^{-} + \cdot OH \qquad \text{(xi)}$$

$$Co^{+3} + ROOH \longrightarrow ROO\cdot + Co^{+2} + H^{+} \qquad \text{(xii)}$$

$$ROO\cdot + RH \longrightarrow ROOH + R\cdot \qquad \text{(xiii)}$$

$$R\cdot + O_2 \longrightarrow RCO\cdot \qquad \text{(xiv)}$$

$$ROO\cdot + RCO\cdot \longrightarrow \text{inert products} \qquad \text{(xv)}$$

Equation (xi) serves to reoxidize the cobaltous ion, and since the reaction is rapid, is not rate determining.

It may be mentioned here that the interpretation of Kharasch (66) on the role of cobalt ions is in complete accord with the above equations.

These equations, however, belong more properly in the discussion of metal-catalyzed decomposition of hydroperoxides and are further mentioned there. Their importance here is to demonstrate that metal ions initiate chains indirectly by bringing about the production of free radicals from hydroperoxide molecules.

Propagation

The propagation steps in autoxidation are presented in equations (ii) and (iii). Reaction (ii) is very rapid, while the cleavage of the R-H bond in (iii) by $ROO\cdot$ does not occur so readily (72).

Termination

Equations (iv), (v), and (vi) represent three of the possible mechanisms by which autoxidation chains can be terminated. A more complete list was suggested by Robertson and Waters (28):

$$R\cdot + R\cdot \longrightarrow RH + R(-H) \tag{iv}$$

$$ROO\cdot + \cdot OH \longrightarrow ROH + O_2 \tag{v}$$

$$R\cdot + R\cdot \longrightarrow RR \tag{vi}$$

$$ROO\cdot + ROO\cdot \longrightarrow ROOOOR \tag{xvi}$$

$$R\cdot + ROO\cdot \longrightarrow ROOR \tag{xvii}$$

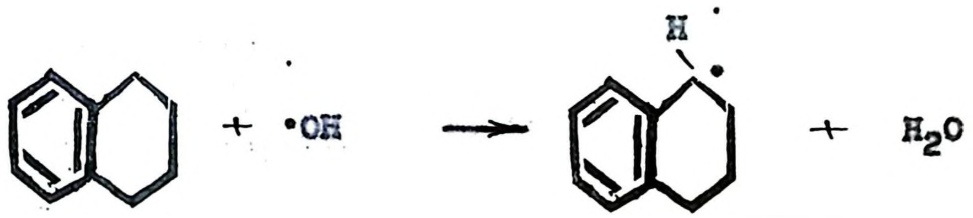
$$R\cdot + \cdot OH \longrightarrow ROH \tag{xviii}$$

$$R\cdot + \text{inhibitor} \longrightarrow \text{inert products} \tag{xix}$$

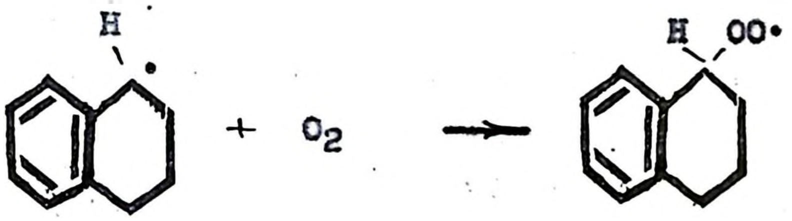
$$ROO\cdot + \text{inhibitor} \longrightarrow \text{inert products} \tag{xx}$$

Some of these are worthy of further comment. The disproportionation reaction (iv) is always operative in tetralin oxidation, and 1,2-dihydronaphthalene is found in the products. Since tetralin hydroperoxide has been catalytically decomposed to give approximately equivalent amounts of α-tetralol and oxygen, reaction (v) has been considered by these workers as very important in tetralin autoxidation. In regard to reaction (vi), no ditetralyl has been found in the autoxidation products from tetralin, but its analogue has been found in the products of the autoxidation of ethylbenzene (29). Reaction (xvi) is very unlikely. Reaction (xvii) is certainly possible, but the peroxide formed would be a fresh autoxidation catalyst since it would readily decompose into radicals.

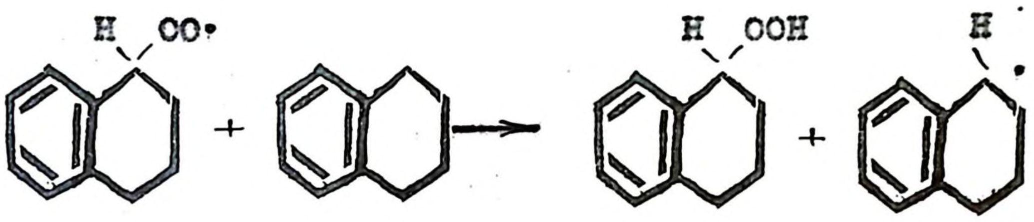
Robertson and Waters (28), after studying both the catalyzed decomposition of tetralin hydroperoxide, and the uncatalyzed oxidation of tetralin, concluded that the main reaction sequence can be represented:



(xxi)



(xxii)



(xxiii)

(xxiv)

The views of Kharasch on cumene hydroperoxide decomposition do not parallel those of Robertson and Waters on tetralin hydroperoxide. The uncatalyzed thermal decomposition of pure cumene hydroperoxide in cumene (61) affords no evidence that the •OH radical is more active in chain initiation than RO• radicals (see equation (xxi)). In fact, when the hydroperoxide was decomposed in the presence of metal ions, strong evidence was obtained for the existance of RO• radicals but not •OH radicals (65).

The interpretation given by Kharasch for oxygen evolution is therefore quite different from equations (v) and (xxiv). Production of oxygen is stated by Kharasch (66) to be possible only in the presence of certain oxidants or of bases. However, in a discussion of the thermal decomposition of cumene hydroperoxide in the presence of alcohols such as dimethylphenylcarbinol (61), he indicates that the alcohols can act as bases (see Thermal Decomposition into Free Radicals, p.29). According to Kharasch, peroxy radicals

(ROO•) are not involved, but rather hydroperoxide and alcohol molecules, so that the production of oxygen is not a chain-terminating step.

Emerson (29) studied the catalytic autoxidation of ethylbenzene, and concluded that RO• radicals are the chief initiators of secondary oxidation chains and not •OH radicals.

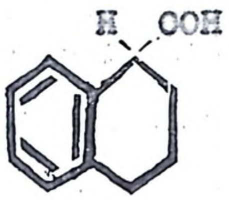
It is quite evident that this discussion is beginning to invade the realm of Hydroperoxide Decomposition. Suffice it to say that since Robertson and Waters (28) were able to collect evolved oxygen, while Emerson (29) did not mention oxygen at all, more than one mechanism may be involved. In Kharasch's group of papers it is pointed out more than once that erroneous conclusions can easily be drawn in these oxidation studies. Reactions proceeding by several mechanisms are sometimes superimposed upon one another. Different hydrocarbons do not behave alike. Impurities can cause added effects to an otherwise straightforward reaction.

Point of Oxidative Attack

Walsh (73, 74) has noted that the tertiary C-H bond is attacked in preference to the secondary bond, and the secondary in preference to the primary. Stephens (14) found that alkylbenzenes were oxidized at the α-carbon atom in every case. Both of these rules are consistant with a general prediction that the most stable free radical will be the one formed.

The oxidative attack on an olefin has been shown to occur at the activated methylene group adjacent to the double bond (30, 54, 55, 75). Thus, the hydroperoxides of several hydrocarbons already mentioned are as follows:

Cyclohexene
hydroperoxide

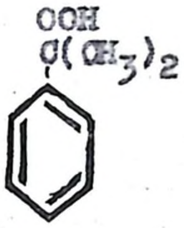


Tetralin
hydroperoxide

Decalin
hydroperoxide

Ethylbenzene
hydroperoxide

p-Xylene
hydroperoxide



Cumene
hydroperoxide

Step 2 - Hydroperoxide Decomposition

Although some of the mechanisms discussed under Step 1 are complex, the essential reactions representing hydroperoxide formation are simple and are generally accepted. This cannot be said of the decomposition of hydroperoxides. As pointed out by Waters (8), the mechanism is strongly dependent on the environment. The truth of this statement is vividly amplified in the recent series of papers by Kharasch and his colleagues (40, 41, 58 to 67 incl.).

Not only can the decomposition of a hydroperoxide proceed by either free radical or ionic mechanisms, but the decomposition can be profoundly influenced by the presence of certain types of compounds.

Kharasch (40) points out that three independent types of decomposition may be effected depending on the methods used:

(a) Acid-catalyzed decomposition, which proceeds by an ionic mechanism.

(b) Decomposition into free radicals.

(c) Decomposition by a reagent which causes evolution of oxygen.

Furthermore, the decomposition into free radicals may be brought about:

(i) Thermally (61).

(ii)By means of heavy metal catalysts (41).

And the decomposition accompanied by the evolution of oxygen (66) may be caused:

(i) By an oxidant capable of abstracting one electron.

(ii) By heating a tertiary hydroperoxide with alkali.

(iii) By treating a hydroperoxide with an "additive" and alkali at room temperature.

Each of the methods of hydroperoxide decomposition will now be discussed in some detail. It is important to remember that unless conditions are carefully controlled, more than one mechanism can be operative at one time.

Acid-Catalyzed Decomposition

It may be shown by many examples that the mechanism of hydroperoxide decomposition in the presence of strong acids is ionic in nature. Cleavage of the O-O bond leads to an oxonium ion which is stabilized by a rearrangement of a hydrocarbon group with accompanying scission of the C-C bond.

Hock (12) treated pure cumene hydroperoxide with dilute sulphuric acid and obtained as products, phenol and acetone, as well as some dimethylphenylcarbinol. The mechanism suggested by Kharasch (40) is as follows:

$$C_6H_5(CH_3)_2COOH + \text{Acid} \longrightarrow C_6H_5(CH_3)_2CO^+ + ACH \qquad \text{(xxv}$$

$$C_6H_5(CH_3)_2CO^+ \longrightarrow (CH_3)_2\overset{+}{C}OC_6H_5 \qquad \text{(xxvi)}$$

$$(CH_3)_2\overset{+}{C}OC_6H_5 + C_6H_5(CH_3)_2COOH \longrightarrow (CH_3)_2(OH)COC_6H_5 + C_6H_5(CH_3)_2CO^+ \qquad \text{(xxvii)}$$

$$(CH_3)_2(OH)COC_6H_5 \longrightarrow C_6H_5OH + (CH_3)_2CO \qquad \text{(xxviii)}$$

Kharasch (40) and his associates have pointed out that reagents and reaction conditions are extremely important in acid-catalyzed decompositions, and that in some cases, particularly at high temperatures, other mechanisms can superimpose on the ionic decomposition. To avoid this a general method for carrying out exclusively ionic disintegrations of hydroperoxides was worked out in which the hydroperoxides are dissolved in glacial acetic acid and are decomposed by adding a small amount of perchloric acid.

Under these conditions, cumene hydroperoxide decomposed quantitatively to phenol and acetone. Several other hydroperoxides were prepared in pure form, and were decomposed in the same manner (62, 63).

<u>α-Phenylethyl hydroperoxide</u> (62) decomposed at 20-25° C. to yield phenol and acetaldehyde, but no acetophenone. Therefore the phenyl was the migrating group.

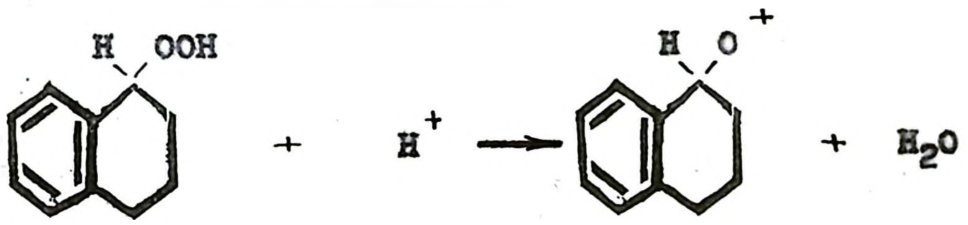
$$C_6H_5CH(CH_3)OOH \xrightarrow{H^+} C_6H_5CH(CH_3)O^+ \qquad \text{(xxix)}$$

$$C_6H_5CH(CH_3)O^+ \longrightarrow (CH_3)\overset{+}{C}HOC_6H_5 \qquad \text{(xxx)}$$

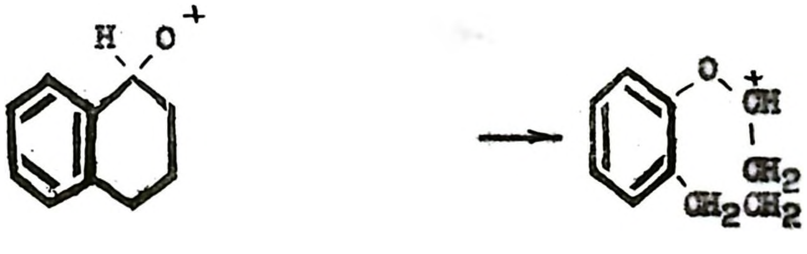
$$(CH_3)\overset{+}{C}HOC_6H_5 + C_6H_5CH(CH_3)OOH \longrightarrow CH_3CHO + C_6H_5OH + C_6H_5CH(CH_3)O^+ \qquad \text{(xxxi)}$$

At higher temperatures more complex products were also obtained.

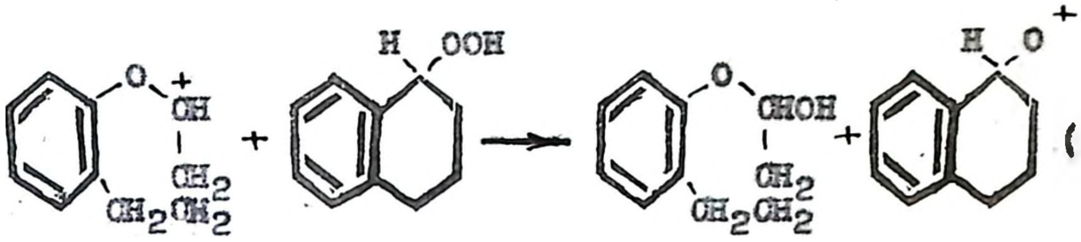
<u>1-Tetralyl hydroperoxide</u> (63) decomposed principally to the aldol of γ-(o-hydroxyphenyl)butyraldehyde.



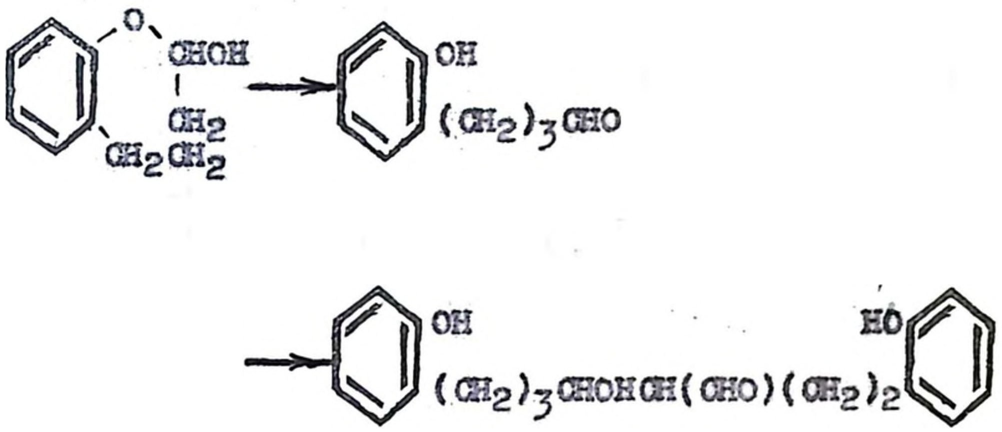
(xxxii)



(xxxiii)

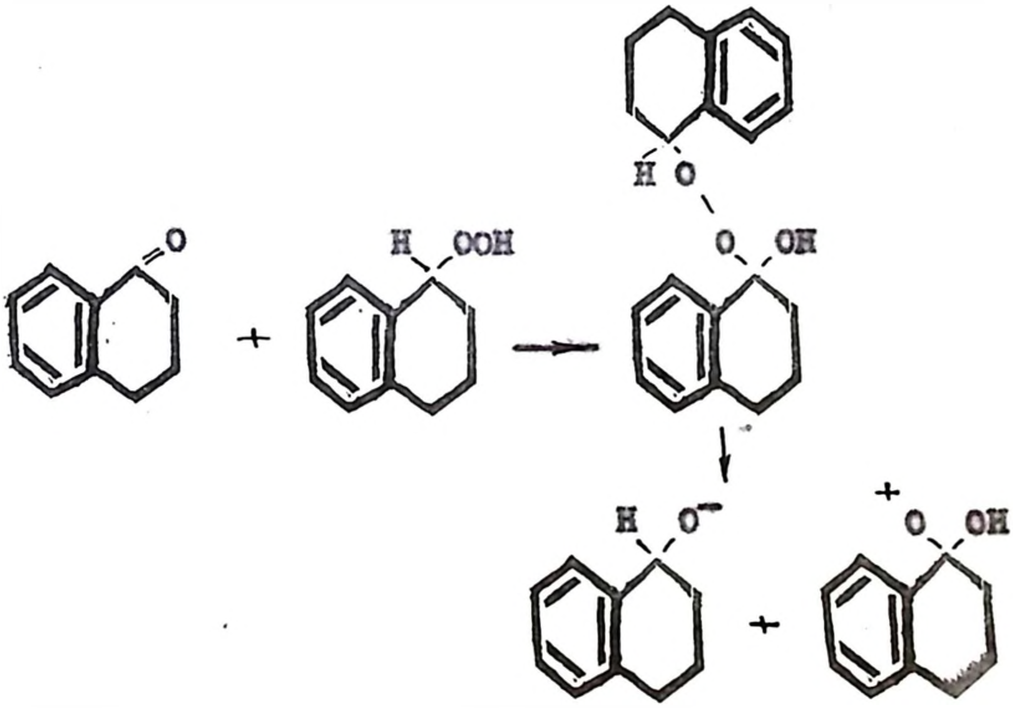


(xxxiv)

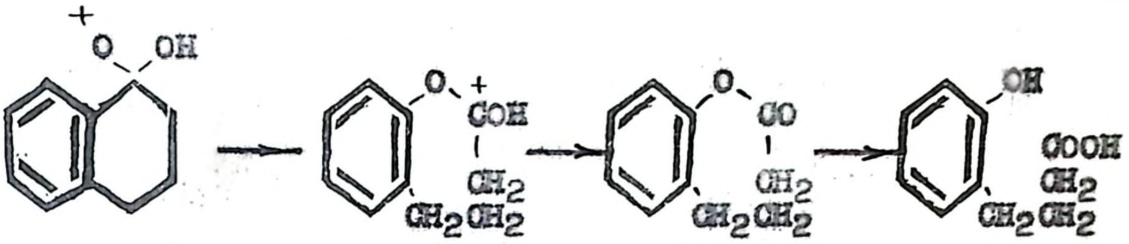


(xxxv)

Robertson and Waters (26), some years previously, obtained a small amount of γ-(*o*-hydroxyphenyl)butyric acid from an oxidation of tetralin. They proposed an ionic mechanism involving the action of hydroperoxide on α-tetralone.



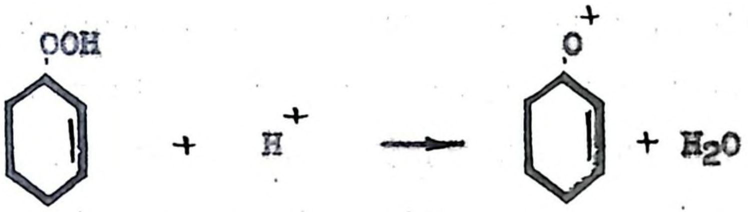
(xxxvi)



(xxxvi a)

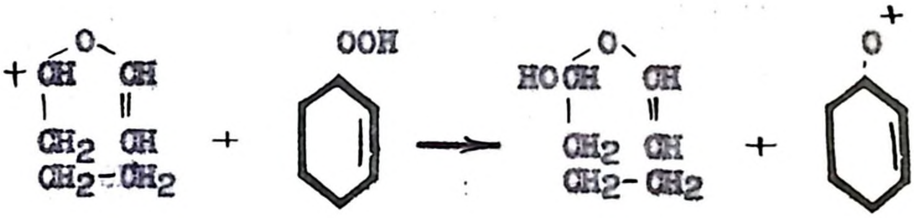
γ-(o-Hydroxyphenyl)butyric acid was more likely produced, however, from the oxidation of the corresponding aldehyde, which in turn was a product of hydroperoxide decomposition as per equations (xxxii) to (xxxv) inclusive.

3-Cyclohexenyl hydroperoxide (63) decomposed to the expected products, adipaldehyde and cyclopentene-1-carboxaldehyde.

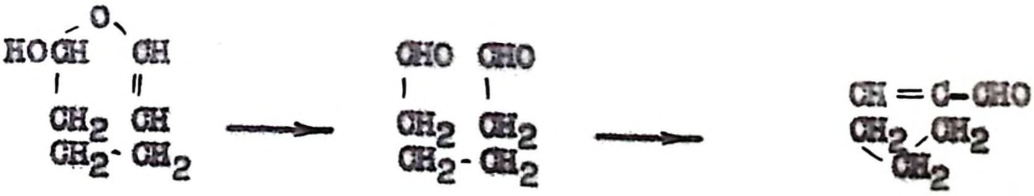


(xxxvii)

(xxxviii)

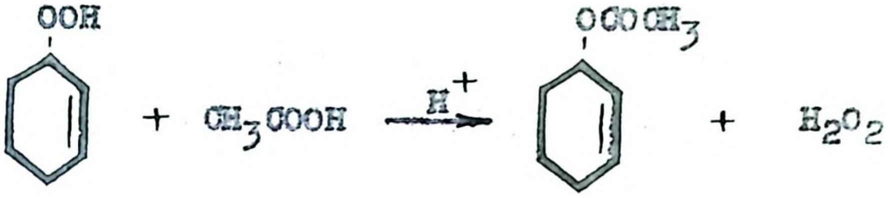


(xxxix)

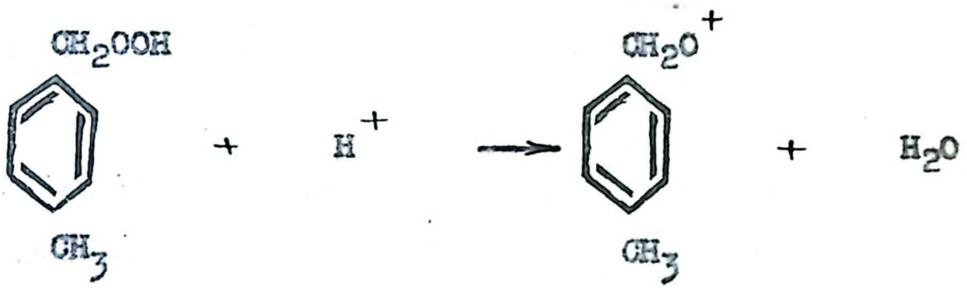


(xl)

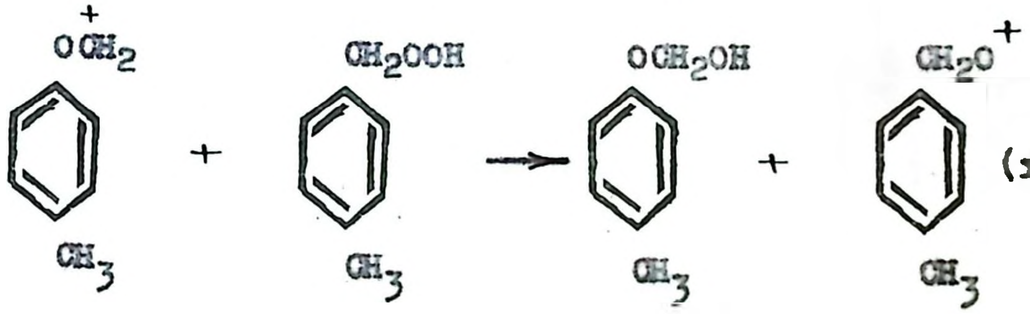
Some 3-cyclohexenyl acetate is also produced, likely by the metathetical reaction between the hydroperoxide and the solvent, acetic acid.

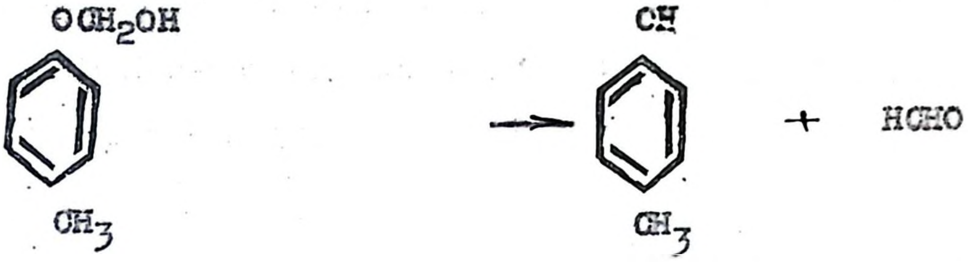

(xli)

α-*p*-Xylyl hydroperoxide (63) decomposed under similar acidic conditions to the expected products, formaldehyde and *p*-cresol, to the extent of only 38 per cent. *p*-Tolualdehyde (61 per cent) was also formed, presumably by a non-ionic thermal decomposition.


(xlii)


(xliii)


(xliv)



(xlv)

p-Nitrotriphenylmethyl hydroperoxide was decomposed with strong acid by Bartlett and Cotman (76), and quantitative yields of p-nitrobenzophenone and phenol were obtained. This means that a phenyl radical migrated to the total exclusion of p-nitrophenyl.

$$\begin{matrix} NO_2C_6H_5\diagdown \\ C_6H_5-CO^+ \\ C_6H_5\diagup \end{matrix} \longrightarrow \begin{matrix} NO_2C_6H_5\diagdown \\ C_6H_5\diagup \end{matrix}\overset{+}{C}OC_6H_5$$

(xlvi)

This result is consistent with theoretical considerations, for nitrobenzene is deactivated to cationic attack in comparison to benzene.

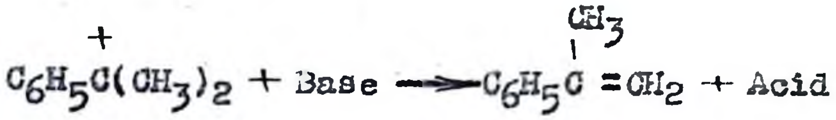
The foregoing examples indicate that when a pure hydroperoxide is isolated and treated with acid, the products can usually be predicted. A hydroperoxide in an oxidation mixture is naturally subjected to many more influences. Kharasch has shown that only strong acids in the Lewis sense, i.e., the electron acceptor sense, cause such ionic decomposition. Thus, ferric chloride, boron trifluoride, aluminum chloride, and sulphuric acid in such solvents as benzene and dioxane give results identical with those obtained by the use of perchloric acid and acetic acid.

It has been reported (3, 77) that the process for the commercial manufacture of phenol and acetone from cumene, patented by the Hercules Powder Co. (78, 79) in the United States, involves a free radical mechanism rather than the ionic mechanism. This is unlikely. Furthermore, although Fordham and Williams (39) report the decomposition of cumene hydroperoxide to phenol and acetone by a free radical mechanism, Kharasch (61) points out that their unusual results may be explained on the basis of impure materials.

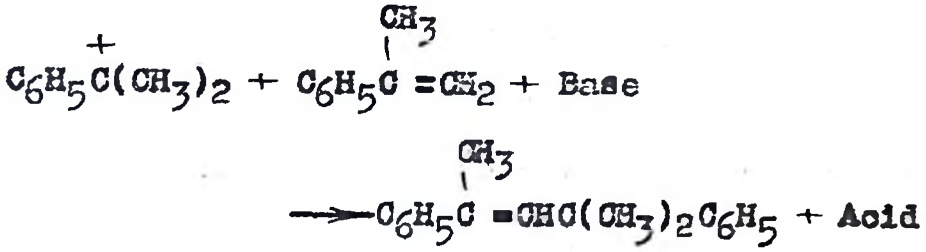
Commercial production of phenol and acetone from cumene has been patented also in Great Britain (43). The first plant-scale operations anywhere in the world have recently been initiated in Canada by B.A.-Shawinigan Ltd. Cumene from a petroleum source is oxidized with air in the presence of aqueous alkali, and the resultant hydroperoxide is decomposed with sulphuric acid.

In his study of the acid-catalyzed decomposition of cumene hydroperoxide, Kharasch (40) found that the presence of dimethylphenylcarbinol decreased the formation of phenol and acetone, and caused a corresponding formation of 2,4-diphenyl-4-methyl-2-pentene (dimer of α-methylstyrene). The explanation advanced was that the carbinol is a stronger base than the hydroperoxide, and these reactions were postulated:

$$C_6H_5COH(CH_3)_2 + \text{Acid} \longrightarrow C_6H_5\overset{+}{C}(CH_3)_2 + H_2O + \text{Base} \quad \text{(xlvii)}$$



$$C_6H_5\overset{+}{C}(CH_3)_2 + \text{Base} \longrightarrow C_6H_5\overset{\overset{CH_3}{|}}{C}{=}CH_2 + \text{Acid} \qquad \text{(xlviii)}$$



$$C_6H_5\overset{+}{C}(CH_3)_2 + C_6H_5\overset{\overset{CH_3}{|}}{C}{=}CH_2 + \text{Base} \longrightarrow C_6H_5\overset{\overset{CH_3}{|}}{C}{=}CHC(CH_3)_2C_6H_5 + \text{Acid} \qquad \text{(xlix)}$$

Furthermore, when dimethylphenylcarbinol was treated with hydrogen peroxide in the presence of strong acid (no hydroperoxide being present to start with), a quantitative yield of phenol and acetone was obtained. The following mechanism was postulated:

$$C_6H_5(CH_3)_2COH + \text{Acid} \longrightarrow C_6H_5(CH_3)_2\overset{+}{C} + \text{Base} + H_2O \qquad \text{(xlvii)}$$

$$C_6H_5(CH_3)_2\overset{+}{C} + \text{Base} + H_2O_2 \longrightarrow C_6H_5(CH_3)_2COOH + \text{Acid} \qquad \text{(l)}$$

$$C_6H_5(CH_3)_2COOH + \text{Acid} \longrightarrow C_6H_5(CH_3)_2C\overset{+}{O} + \text{Base} + H_2O \qquad \text{(li)}$$

This mechanism can also be used to explain the occurrence of the carbinol in the product of Hock's <u>dilute</u> acid-catalyzed decomposition of cumene hydroperoxide already mentioned (12).

$$C_6H_5(CH_3)_2COOH + \overset{+}{H} \longrightarrow C_6H_5(CH_3)_2\overset{+}{C} + H_2O_2 \qquad \text{(lii, reverse l)}$$

$$C_6H_5(CH_3)_2\overset{+}{C} + \text{Base} + H_2O \longrightarrow C_6H_5(CH_3)_2COH + \text{Acid} \qquad \text{(liii, reverse xlvii)}$$

Kharasch repeated this decomposition with dilute sulphuric acid, and demonstrated the presence of hydrogen peroxide in the aqueous portion of the product.

The use of the ionic decomposition of hydroperoxides in the determination of migration aptitudes should be mentioned. The oxonium ion $RR'R''CO^+$ formed from the corresponding hydroperoxide, rearranges to the carbonium ion $R'R''\overset{+}{C}OR$ where R has a greater migrating tendency than either R' or R". Kharasch (59) studied the reaction of tertiary alcohols with hydrogen peroxide in the presence of perchloric acid, and the products obtained indicated in each case the migrating radical. In general, the results showed that migratory aptitude is related to group negativity, e.g., an aryl radical rearranges preferentially to an alkyl group. The rearrangement series obtained agrees essentially with earlier studies on other 1,2-ionic shifts such as the pinacol-pinacolone rearrangement. In fact some discrepancies in the "pinacolone rearrangement series" attributed to steric factors were not observed in the hydroperoxide reaction, for example, o-methoxyphenyl rearranges easier than phenyl as expected from theoretical considerations.

In making some generalizations on acid-catalyzed rearrangement of $RR'R''CO^+$, Kharasch points out that one group must be an aryl radical or its equivalent in activating influence; in fact, tertiary butyl hydroperoxide does not rearrange. In general, susceptibility of ROOH towards acid cleavage of the O-O bond parallels the facility with which hydroperoxides are formed by autoxidation of the corresponding hydrocarbons.

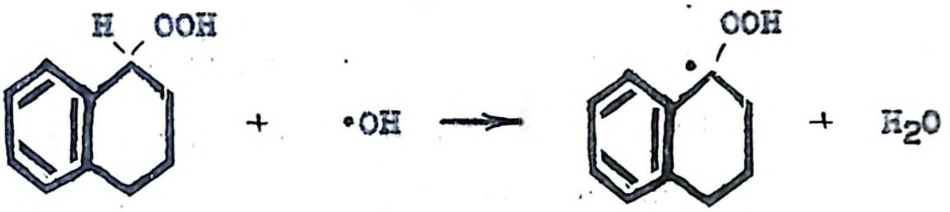
Thermal Decomposition into Free Radicals

In the discussion of hydroperoxide formation it has already been mentioned that hydroperoxides can split into the free radicals RO• and •OH, each of which can initiate secondary oxidation chains by abstracting a hydrogen from the hydrocarbon. The breakdown into radicals may be promoted by light or heat. Thermal stability parallels the ease of formation; thus, tertiary hydroperoxides are most stable, secondary next, and primary least. Carefully purified cumene hydroperoxide in purified cumene is relatively stable at 100° C.; little or no decomposition takes place in forty-eight hours. At 128° C., more than twenty-four hours is necessary for complete decomposition. Conjugation with a double bond also makes for stability. Thus, cyclohexenyl hydroperoxide is quite readily isolated, while cyclohexyl hydroperoxide is known only in solution (3).

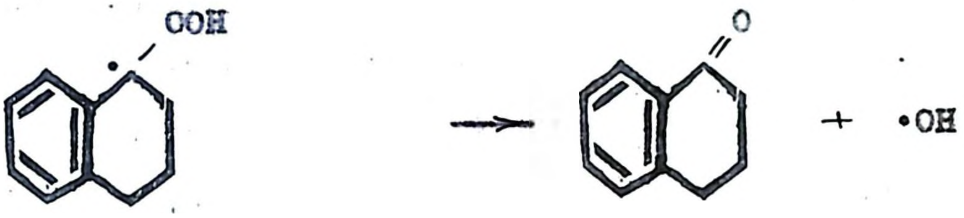
Secondary hydroperoxides such as tetralin hydroperoxide, which have the hydroperoxy group linked to a secondary carbon atom, split readily at the O–O bond. Robertson and Waters (27) studied both the thermal and the metal-ion catalyzed decomposition of tetralin hydroperoxide, and reached conclusions common to both. Although there were strong indications of the homolytic fission of ROOH to RO• and •OH, followed by further reactions of these radicals, about half the tetralin hydroperoxide seemed to decompose according to the simple equation:

(liv)

Robertson and Waters consider that the formation of tetralone is essentially "intramolecular", although at high hydroperoxide concentrations a reaction of hydroperoxide with •OH may occur.



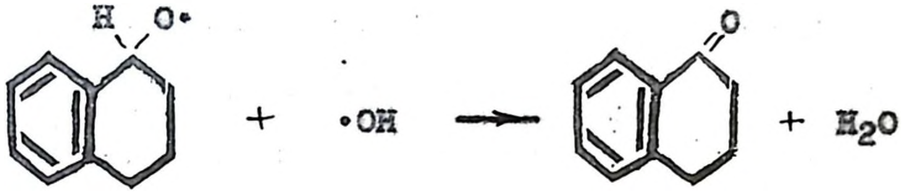
(lv)



(lvi)

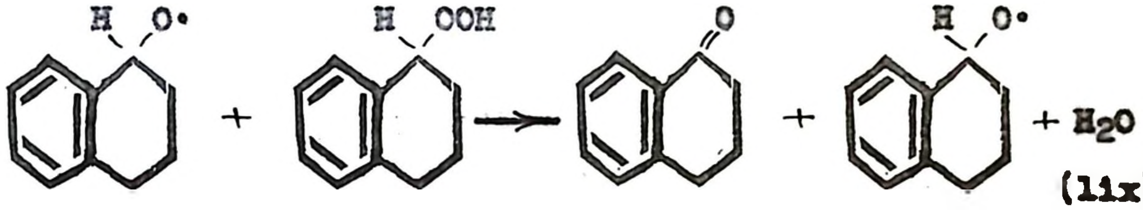
In support of the "intramolecular" mechanism they invoke a theory of Frank and Rabinovitch (80), the essence of which is as follows: When a molecule decomposes into two free radicals in solution, the dissociated fragments tend to be driven together again by the collisions of the surrounding solvent molecules. Only in the exceptional circumstances of their possessing high translational energy are they able to drift far apart before recombining. Equation (liv) can therefore be broken down into:

(lvii)



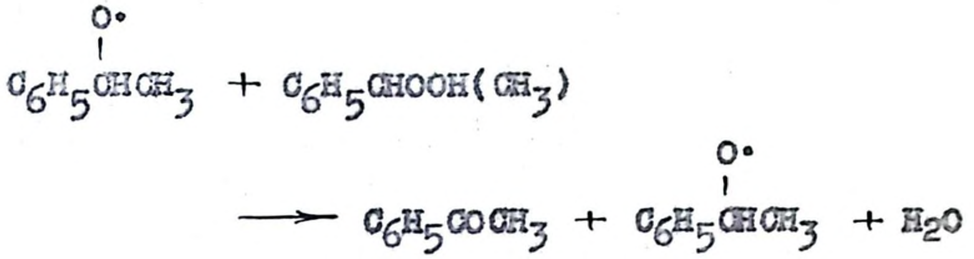
(lviii)

The foregoing mechanisms for α-tetralone production are at variance with the views of Kharasch. He proposed for the free radical decomposition of tetralin hydroperoxide the following (41), in which RO• rather than •OH is the active radical:



(lix)

A similar mechanism was proposed by Kharasch for the decomposition of another secondary hydroperoxide, α-phenylethylhydroperoxide (62):



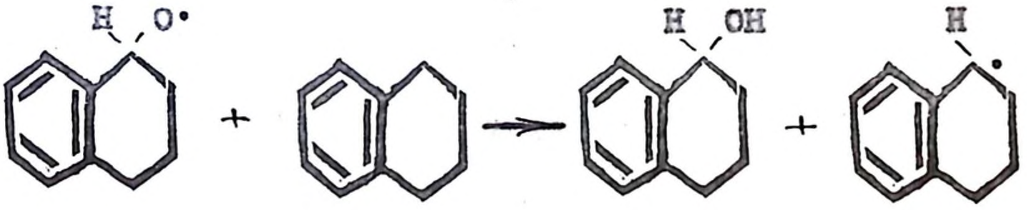
$$C_6H_5\overset{\overset{O\cdot}{|}}{C}HCH_3 + C_6H_5CHOOH(CH_3) \longrightarrow C_6H_5COCH_3 + C_6H_5\overset{\overset{O\cdot}{|}}{C}HCH_3 + H_2O \quad (lx)$$

Both of these equations are based on studies of free radical decompositions catalyzed by ferric ions, and will be discussed again under Metal-Ion Catalyzed Decomposition, p.53.

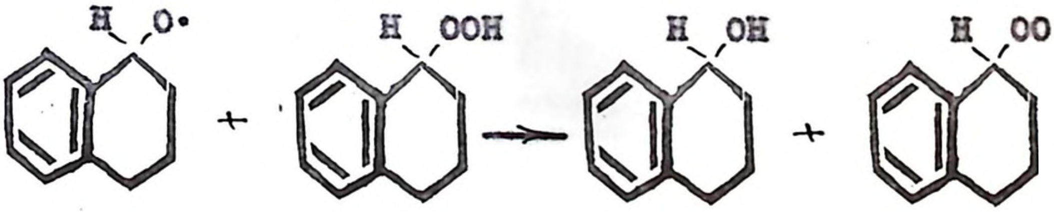
Tertiary hydroperoxides such as cumene are considered by Kharasch (61) to follow under some conditions a similar route to ketone and methanol (see p.42).

$$C_6H_5(CH_3)_2COOH + C_6H_5(CH_3)_2CO\cdot \longrightarrow C_6H_5COCH_3 + C_6H_5(CH_3)_2CO\cdot + CH_3OH \quad (lxi)$$

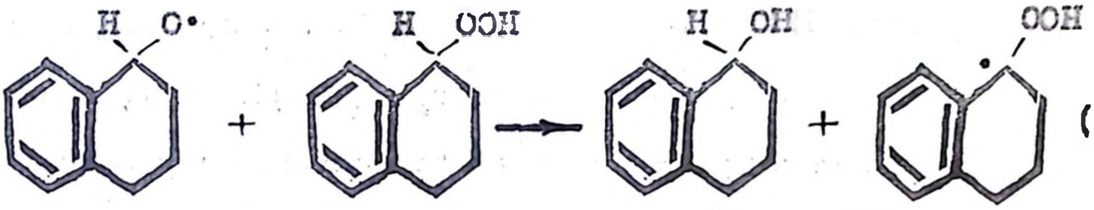
Turning now to carbinol formation, the production of most of the α-tetralol in the thermal decomposition of tetralin hydroperoxide is attributed by Robertson and Waters (27) to oxidation (i.e. dehydrogenation) reactions of the HO· radical. The following equations indicate some of the possible hydrogen donors:



(lxii)



(lxiii)


(lxiv)

In this uncatalyzed thermal decomposition of tetralin hydroperoxide, however, some oxygen was also produced. Therefore, in addition to equations (lxii), (lxiii), and (lxiv), and following directly from (lxiii), Robertson and Waters (27) proposed:


(lxv)

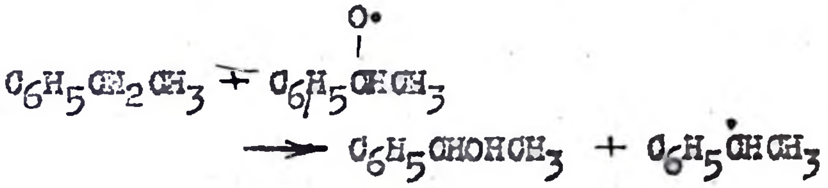
They pointed out that the oxygen was not nearly equivalent to the tetralol, as it was in the metal-ion catalyzed decomposition. As already mentioned, production of oxygen is stated by Kharasch (66) to be possible only in the presence of certain oxidants or bases. However, in a discussion of the thermal decomposition of cumene hydroperoxide in the presence of alcohols like dimethylphenylcarbinol, Kharasch (61) indicates that the alcohols can act as bases. This will presently be elaborated (see equations (xc) ff. p.41).

The autoxidation of ethylbenzene at 140° C. in the presence of chromium oxide was studied by Emerson *et al* (29). The products were acetophenone, 74 per cent, and methylphenylcarbinol, 26 per cent, when water was removed as formed. No oxygen was reported.

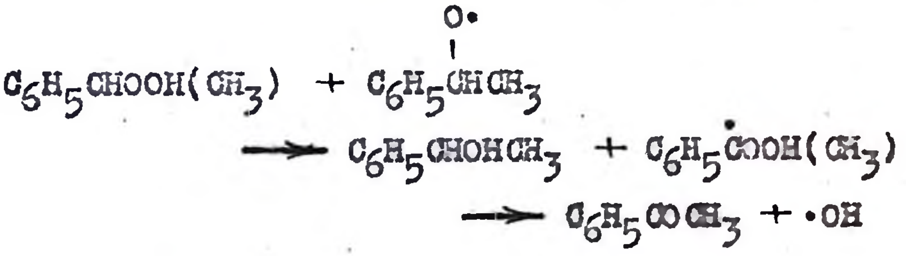
Emerson assumed that α-phenylethyl hydroperoxide was formed by the normal route (see equations (i), (ii), and (iii)), the catalyst being the initiator of the $C_6H_5\dot{C}HCH_3$ radicals. He goes on to point out that at 140°C. the hydroperoxide can be expected to decompose <u>thermally</u> into RO• and •OH radicals, each of which can react with hydrocarbon or hydroperoxide as follows:

$$C_6H_5CH_2CH_3 + \cdot OH \longrightarrow H_2O + C_6H_5\dot{C}HCH_3 \qquad \text{(lxvi)}$$

$$C_6H_5CHOOH(CH_3) + \cdot OH \longrightarrow H_2O + C_6H_5\dot{C}OOH(CH_3)$$
$$\longrightarrow C_6H_5COCH_3 + \cdot OH \qquad \text{(lxvii}$$



$$C_6H_5CH_2CH_3 + C_6H_5\overset{\overset{\textstyle O\cdot}{|}}{C}HCH_3 \longrightarrow C_6H_5CHOHCH_3 + C_6H_5\dot{C}HCH_3 \qquad \text{(lxvi}$$



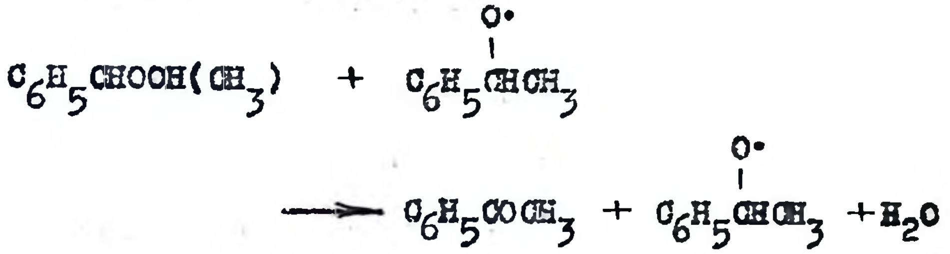
$$C_6H_5CHOOH(CH_3) + C_6H_5\overset{\overset{\textstyle O\cdot}{|}}{C}HCH_3 \longrightarrow C_6H_5CHOHCH_3 + C_6H_5\dot{C}OOH(CH_3)$$
$$\longrightarrow C_6H_5COCH_3 + \cdot OH \qquad \text{(lxix)}$$

The action of •OH in (lxvi) and (lxvii) leads to ketone only, while that of RO• in (lxviii) and (lxix) leads to both ketone and carbinol. Emerson concluded, therefore, that <u>both</u> radicals must be active in the mechanism because reactions represented by (lxvi) and (lxvii) would produce no carbinol, and (lxviii) and (lxix) would lead to more carbinol than ketone. Neither condition was observed.

It was found that when the water produced in the reaction was not removed as formed, production of carbinol was increased and that of ketone decreased, total conversion being unchanged. It was postulated that the influence of the water was a deactivation of ·OH radicals by solution in water, by hydrogen bonding, or some similar phenomenon. Then the resulting increased relative importance of (lxviii) and (lxix) compared to (lxvi) and (lxvii) led to more carbinol. Since the total conversion remained constant, however, it was suggested that ·OH normally played no part in the autoxidation chain, (lxvi), since removal of ·OH must be a chain-terminating reaction. In other words, equation (lxviii) and not (lxvi) was responsible for conversion of hydrocarbon (together with the propagation reaction (iii)), while (lxvii), (lxviii), and (lxix) were all responsible for the products.

This interpretation is very similar to the proposals of Robertson and Waters for the decomposition of tetralin hydroperoxide. Emerson postulated that RO· can abstract a hydrogen from either hydrocarbon or hydroperoxide. Robertson and Waters' equations were similar. Thus (lv) and (lvi) indicate the reaction of ·OH with tetralin hydroperoxide, and (lxii) and (lxiv) represent the abstraction of a hydrogen by RO· from hydrocarbon and hydroperoxide respectively.

It is to be noted, however, that Kharasch's equation (lx) and Robertson and Waters' equation (lviii) indicate two other possible paths to ketone production that Emerson has not considered:



$$C_6H_5CHOOH(CH_3) + C_6H_5\overset{\overset{O\cdot}{|}}{C}HCH_3 \longrightarrow C_6H_5COCH_3 + C_6H_5\overset{\overset{O\cdot}{|}}{C}HCH_3 + H_2O \qquad (lx)$$

and

$$C_6H_5\overset{\overset{O\cdot}{|}}{C}HCH_3 + \cdot OH \longrightarrow C_6H_5COCH_3 + H_2O \qquad (lxx)$$

The former is preferable since positive evidence for •OH radicals has not been presented.

Emerson (29) further found that when 2-5 per cent methylphenylcarbinol was added to the autoxidation mixture ½ - 1½ hours after the reaction temperature had been reached, the resulting product contained the same amount of carbinol as in the oxidations in which no carbinol was added. Total conversion, however, was not changed, The proposal advanced to explain the maintenance of the carbinol/ketone ratio was that carbinol had been oxidized to ketone as follows:

$$C_6H_5CHOHCH_3 + \cdot OH \longrightarrow C_6H_5\dot{C}OHCH_3 + H_2O \qquad (lxxi)$$

$$C_6H_5\dot{C}OHCH_3 + O_2 \longrightarrow C_6H_5CO\dot{O}(OH)(CH_3) \qquad (lxxii)$$

$$C_6H_5CO\dot{O}(OH)(CH_3) + C_6H_5CH_2CH_3 \longrightarrow C_6H_5\dot{C}HCH_3 + C_6H_5COOH(OH)(CH_3) \qquad (lxxiii)$$

$$C_6H_5COOH(OH)(CH_3) \xrightarrow{140^\circ C.} C_6H_5C\dot{O}(OH)(CH_3) + \cdot OH \qquad (lxxiv)$$

$$C_6H_5C\dot{O}(OH)(CH_3) + C_6H_5CH_2CH_3 \rightleftharpoons C_6H_5\dot{C}HCH_3 + [C_6H_5COH(OH)(CH_3)] \qquad (lxxv)$$

$$[C_6H_5COH(OH)(CH_3)] \longrightarrow C_6H_5COCH_3 + H_2O \qquad (lxxvi)$$

This interpretation of the results can be criticized on two counts. Firstly, an alternative explanation for the unchanged carbinol/ketone ratio might be given. The added carbinol possibly retarded or affected equilibrium in those mechanisms leading to carbinol as a product, and affected them to a point where the carbinol/ketone ratio was identical with the usual ratio. Secondly, it might be considered that carbinol is converted to ketone, but by another mechanism. Kharasch (41) studied the decomposition of α-cumyl hydroperoxide in the presence of the corresponding carbinol, and reached conclusions which might apply here. It was postulated that carbinol was converted to RO· and thence to ketone, but by a much more plausible mechanism than that given above for methylphenylcarbinol. (see equation (lxxxviii) ff. p.40.)

In any case, it is of interest that Emerson and Lucas (35) were issued a patent for the production of acetophenone from ethylbenzene, in which a prime feature was the separation of methylphenylcarbinol from the product, and the return of this to the next batch for conversion to more acetophenone.

Tertiary hydroperoxides, according to George and Walsh (36), decompose first at the O-O bond, and then at the weakest C-C bond to yield a ketone.

$$C_6H_5(CH_3)_2COOH \longrightarrow C_6H_5(CH_3)_2CO\cdot \longrightarrow C_6H_5COCH_3 + CH_3\cdot \qquad \text{(lxvii)}$$

$$C_6H_5(CH_3)(C_2H_5)COOH \longrightarrow C_6H_5(CH_3)(C_2H_5)CO\cdot \longrightarrow C_6H_5COCH_3 + C_2H_5\cdot \qquad \text{(lxviii)}$$

The work of Stephens and Rotuda (37) on various tertiary hydroperoxides bears this out. Ketones, however, are not the only compounds formed, as further examples will show. As in the case of secondary hydroperoxides, many reactions must be proposed to account for the various products.

Kharasch (41) and his colleagues have studied the decomposition of cumene hydroperoxide in hydrocarbon solvents (cumene and ethylbenzene), in solvents that induced decomposition (alcohols and olefins), and in acids (acetic and benzoic). The first two of these three studies are of interest in a consideration of autoxidation. In the oxidation of cumene, for instance, cumene hydroperoxide decomposes in the presence of both the starting material, cumene, and the products, including the alcohol dimethylphenylcarbinol.

Cumene hydroperoxide was decomposed at 70-100° C. in cumene with a little acetyl peroxide as catalyst. Free radicals from acetyl peroxide produced α-cumyl radicals, which in turn reacted with the hydroperoxide. A variety of products were produced including dimethylphenylcarbinol, acetophenone, methane, the dimer from α-cumyl radicals, but no oxygen. The reaction scheme proposed by Kharasch (61) is as follows:

$$C_6H_5(CH_3)_2COOH + C_6H_5(CH_3)_2C\cdot \longrightarrow \text{Complex A} \qquad \text{(lxxix)}$$

$$\text{Complex A} + C_6H_5(CH_3)_2CH \longrightarrow 2\ C_6H_5(CH_3)_2COH + C_6H_5(CH_3)_2C\cdot \qquad \text{(lxxx)}$$

$$C_6H_5(CH_3)_2COOH \longrightarrow C_6H_5(CH_3)C\underset{O}{\diagdown\diagup}CH_2 + H_2O \qquad \text{(lxxxi)}$$

$$C_6H_5(CH_3)_2COOH \longrightarrow C_6H_5(CH_3)_2CO\cdot + \cdot OH \qquad \text{(lxxxii)}$$

$$C_6H_5(CH_3)_2CO\cdot \longrightarrow C_6H_5COCH_3 + CH_3\cdot \qquad \text{(lxxxiii)}$$

$$CH_3\cdot + C_6H_5(CH_3)_2CH \longrightarrow CH_4 + C_6H_5(CH_3)_2C\cdot \qquad \text{(lxxxiv)}$$

$$\cdot OH + C_6H_5(CH_3)_2CH \longrightarrow H_2O + C_6H_5(CH_3)_2C\cdot \qquad \text{(lxxxv)}$$

$$C_6H_5(CH_3)_2CO\cdot + C_6H_5(CH_3)_2CH \longrightarrow C_6H_5(CH_3)_2COH + C_6H_5(CH_3)_2C\cdot \qquad \text{(lxxxvi)}$$

$$2\ C_6H_5(CH_3)_2C\cdot \longrightarrow C_6H_5(CH_3)_2C\text{-}C(CH_3)_2C_6H_5 \qquad \text{(lxxxvii)}$$

Reactions (lxxix) and (lxxx) for the production of the carbinol product are quite different from those suggested by previous workers. "The formation of an epoxide in (lxxxi) is postulated because the reaction products react in the cold with lead tetraacetate."

In addition to the products already noted, small equimolar quantities (6 per cent) of phenol and acetone were produced. This makes it necessary to assume that a slight ionic reaction accompanied the thermal decomposition. This conclusion is supported by the fact that small amounts of alkaline material in the mixture tended to suppress phenol and acetone production.

Cumene hydroperoxide was also decomposed in the presence of dimethylphenylcarbinol, and Kharasch (41) reported that the data obtained could be interpreted by assuming that decomposition occurred in two mutually independent ways.

Firstly, decomposition occurred by preliminary formation of α-cumyl peroxide, less stable than the hydroperoxide:

$$C_6H_5(CH_3)_2COOH + C_6H_5(CH_3)_2COH \longrightarrow C_6H_5(CH_3)_2CO\text{-}OC(CH_3)_2C_6H_5 + H_2O \qquad \text{(lxxxviii)}$$

$$C_6H_5(CH_3)_2CO\text{-}OC(CH_3)_2C_6H_5 \longrightarrow 2\ C_6H_5(CH_3)_2CO\cdot \qquad \text{([illegible])}$$

followed by:

$$C_6H_5(CH_3)_2CO\cdot + C_6H_5(CH_3)_2COOH \longrightarrow C_6H_5COCH_3 + CH_3OH + C_6H_5(CH_3)_2CO\cdot \qquad \text{(lxi)}$$

According to this mechanism, the decomposition of hydroperoxide was induced by decomposition of the peroxide formed in (lxxxviii), and was not brought about by primary breakup of hydroperoxide itself into radicals. Furthermore, it is postulated that (lxxxviii) proceeds by an ionic mechanism. In support of this it was found that addition of α-cumyl chloride increased the formation of peroxide (α-cumyl chloride supplying excess R^+ ions), and that small amounts of alkali decreased the rate of thermal decomposition at 100° C. in carbinols (alkali tending to reduce the concentration of R^+ ions).

<u>Secondly</u>, decomposition of α-cumyl hydroperoxide in dimethylphenylcarbinol proceeded to carbinol and oxygen:

$$C_6H_5(CH_3)_2COOH + C_6H_5(CH_3)_2COH \longrightarrow C_6H_5(CH_3)_2COO^- + C_6H_5(CH_3)_2C\overset{+}{O}H_2 \quad \text{(xc)}$$

$$C_6H_5(CH_3)_2COO^- + C_6H_5(CH_3)_2COOH \longrightarrow C_6H_5(CH_3)_2COH + C_6H_5(CH_3)_2CO^- \quad O_2 \quad \text{(xci)}$$

An alternative possibility for oxygen formation could be hydrolysis of hydroperoxide followed by decomposition of the hydrogen peroxide thus formed. (see Base-Catalyzed Decomposition, p.46)

$$C_6H_5(CH_3)_2COOH + H_2O \longrightarrow C_6H_5(CH_3)_2COH + H_2O_2 \quad \text{(xcii)}$$

$$H_2O_2 \longrightarrow H_2O + \tfrac{1}{2}O_2 \quad \text{(xcii a)}$$

It has already been mentioned that Robertson and Waters (27) obtained oxygen in the thermal decomposition of tetralin hydroperoxide, and that this may be due to the action of carbinol products as bases. More difficult to account for are the results of Milas and Surgenor (81) with tertiary butyl hydroperoxide. They heated the pure hydroperoxide at $95\text{-}100^{\circ}$ C. without a solvent, and obtained smooth conversion to tertiary butyl alcohol accompanied by the evolution of oxygen. No measure of the amount of oxygen was made. In view of the absence of hydrocarbon, carbinol, and catalysts, a direct homolytic fission into free radicals was a most likely first step, followed possibly by the following:

$$(CH_3)_3CO\cdot + (CH_3)_3COOH \longrightarrow (CH_3)_3COH + (CH_3)_3COO\cdot \qquad \text{(xciii)}$$

$$(CH_3)_3COO\cdot + \cdot OH \longrightarrow (CH_3)_3COH + O_2 \qquad \text{(xciv)}$$

These are analogous to Robertson and Waters' (27) suggested reactions of α-tetralyloxy radicals, (lxiii) and (lxv) respectively.

To return to the discussion on induced hydroperoxide decomposition in carbinol solvents, the presence of equation (lxi) in this reaction scheme is quite logical. Its absence from the equations proposed by Kharasch for decomposition in hydrocarbon solvents, (lxxix) to (lxxxvii) inclusive, however, is somewhat puzzling. Presumably methanol was not isolated from the products of the decomposition under these conditions.

It is of interest in this regard that Kharasch (61) decomposed α-cumyl peroxide in a hydrocarbon solvent and obtained equivalent amounts of acetophenone and methane.

$$C_6H_5(CH_3)_2CO\cdot + RH \longrightarrow R\cdot + CH_4 + C_6H_5COCH_3 \quad \text{(xcv)}$$

But with added hydroperoxide, below 120°C., this did not occur. Instead, methanol was produced together with acetophenone by the chain mechanism involving RO• and ROOH, as per equation (lxi). At 140°C. and over, however, RO• is unstable, and even in the presence of hydroperoxide, the products are acetophenone and methane in equivalent quantities. In view of these results, then, it is difficult to understand why Kharasch considers equation (lxi) is inoperative in the thermal decomposition of α-cumyl hydroperoxide in cumene at 70-100°C.

It has already been mentioned that Kharasch (59) has studied the migratory aptitudes of various groups by means of the ionic rearrangement of hydroperoxides. It is of interest to note in this discussion on Decomposition into Free Radicals that Kharasch (64) has made similar studies with free radical rearrangements. Both organic cations and free radicals are stabilized by elimination or rearrangement.

$$RR'R''CO^{+} \longrightarrow RCOR' + R''^{+} \quad \text{(elimination)} \quad \text{(xcvi)}$$

$$RR'R''CO^{+} \longrightarrow RR'\overset{+}{C}OR'' \quad \text{(rearrangement)} \quad \text{(xcvii)}$$

$$RR'R''CO\cdot \longrightarrow RCOR' + R''\cdot \quad \text{(elimination)} \quad \text{(xcviii)}$$

$$RR'R''CO\cdot \longrightarrow RR'\overset{\bullet}{C}OR'' \quad \text{(rearrangement)} \quad \text{(xcix)}$$

In cationic reactions of α-cumyl and α-phenylethyl hydroperoxides, migration was preferred over elimination (40, 62), whereas in the free radical reactions, elimination was predominant (41, 61, 62).

Bartlett and Cotman (76) studied the thermal decomposition of a hydroperoxide yielding an $Ar_2Ar'CO\cdot$ radical, namely p-nitrophenyldiphenylmethyl hydroperoxide. Results obtained were confusing, and, as Kharasch (64) points out, could only be ambiguous since products obtained could result from either elimination or rearrangement. This can be illustrated as follows:

$$\begin{tikzcd} & Ar'Ar''\dot{C}OAr \arrow[r, "ArAr'Ar''COOH"] & Ar'COAr'' + ArOH + ArAr'Ar''CO\cdot \qquad (c) \\ ArAr'Ar''CO\cdot \arrow[ur, "(migration)"] \arrow[dr, "(elimination)"'] & & \\ & Ar'COAr'' + Ar\cdot \arrow[r, "ArAr'Ar''COOH"] & Ar'COAr'' + ArOH + ArAr'Ar''CO\cdot \qquad (ci) \end{tikzcd}$$

The presence of the hydroperoxide makes both of the above reactions possible. If the source of the RO· radicals is a <u>peroxide</u> instead, however, the results are unambiguous. Kharasch decomposed tert-butylheterotriarylmethyl peroxides in cumene solution and obtained products formed from α-cumyl radicals and <u>rearranged</u> triarylmethyl radicals.

$$(CH_3)_3CO{-}OCArAr'Ar'' \longrightarrow (CH_3)_3CO\cdot + ArAr'Ar''CO\cdot \qquad (cii)$$

$$ArAr'Ar''CO\cdot \longrightarrow Ar'Ar''\dot{C}OAr \qquad (ciii)$$

$$Ar'Ar''\dot{C}OAr + \cdot C(CH_3)_2C_6H_5 \longrightarrow Ar'Ar''(ArO)C{-}C(CH_3)_2C_6H_5 \quad (civ)$$

The final product was identified, and the migrating group was shown clearly from its structure.

In order to make a study of relative migratory aptitudes Kharasch decomposed several of these specially synthesized peroxides from which free radicals of the types $ArAr'Ar''CO\cdot$ and $Ar_2Ar'CO\cdot$ are produced. He showed that the p-biphenyl and α-naphthyl groups will migrate six times faster than a phenyl group, and that a p-tolyl group will migrate about as readily as a phenyl.

The reports of a very early worker in hydrocarbo autoxidation should not be overlooked. Stephens (13, 14, 15, 16, 17, 37) brought about a reaction between alkylbenzenes and molecular oxygen at room temperature by leaving samples of the hydrocarbons in contact with air in large flasks. The action of light over many days brought about exhaustion of the oxygen and conversion to products, chiefly ketones. Ethylbenzene (14) yielded some acetophenone. Cumene (14) was converted to acetophenone, and some formic acid was found as well. p-Cymene (14) yielded chiefly p-methylacetophenone and formic acid, but in addition a little cuminaldehyde and cumic acid were found. Carbinols were not reported.

An explanation of the products is not difficult. The presence of formic acid is obvious enough evidence that oxidation of the one-carbon fragments from cumene and p-cymene has extended far beyond the methanol isolated by Kharasch (equation lxi). The carbinols too were likely formed at first, and then were transformed by further reaction to RO· radicals and to ketones (see equations lxxxviii and lxxxix).

Base-Catalyzed Decomposition

It has been pointed out by Kharasch (66) that hydroperoxides vary widely in their stability towards both dilute and concentrated alkali. Under the influence of alkali most secondary hydroperoxides decompose at or above room temperature to give alcohols, ketones, and other oxidation products. No oxygen evolution has been recorded when primary or secondary hydroperoxides are treated with dilute alkali. On the other hand, tertiary hydroperoxides such as α-cumyl, when treated with alkali, readily yield oxygen.

α-Cumyl hydroperoxide (66) was decomposed relativel slowly when a large excess of alkali was used, much faster with 20 mole per cent alkali. It is thought that ROO^- acts as an oxidant, and attacks undissociated hydroperoxide molecules. In support of this, the sodium salt of α-cumyl hydroperoxide in benzene gives no oxygen when heated to 60-90° C., but decomposes to α-cumyl alcohol (dimethylphenylcarbinol), benzoic acid, and other oxidation products. When free hydroperoxide is added to the solution, however, oxygen is produced, together with α-cumyl alcohol, benzoic acid, and minor byproducts.

$$C_6H_5(CH_3)_2COOH + {}^-OH \longrightarrow C_6H_5(CH_3)_2COO^- + H_2O \qquad \text{(cv)}$$

$$C_6H_5(CH_3)_2COO^- + C_6H_5(CH_3)_2COOH \longrightarrow C_6H_5(CH_3)_2CO^- + C_6H_5(CH_3)_2COH + O_2 \qquad \text{(cvi)}$$

The production of acetophenone, benzoic acid, and other products at 60-100° C. is attributed to the attack of α-cumylperoxy anions (ROO^-) on the carbinol.

Patents (78, 79) have been issued for the liquid-phase oxidation of tertiary alkyl substituted aromatics like cumene and p-cymene in the presence of aqueous alkali. The resulting solution contains about 21 per cent hydroperoxide which is decomposed by slowly distilling in the presence of 4 per cent sodium hydroxide. The resulting products, in the case of p-cymene, are dimethyl-p-tolylcarbinol and p-methylacetophenone, the former comprising 90 per cent of the mixture. From cumene, the analogous carbinol and the same ketone are obtained, the former comprising 74 per cent of the mixture. Production of oxygen is not mentioned.

The nearly quantitative production of carbinol and oxygen from α-cumyl hydroperoxide may be accomplished at room temperature, however, in the presence of dilute alkali and an "additive" (66). Kharasch has done considerable work on a variety of "additives", all of them difunctional compounds capable of forming chelate rings, for example, succinonitrile or phthalonitrile.

The catalytic action of these "additives" is displayed also, whether or not the hydroperoxide is tertiary. Thus, tetralin hydroperoxide dissolved in tert-butyl alcohol can be decomposed with alkali into water, α-tetralone, and higher oxidation products, and the rate of decomposition is doubled by addition of four mole per cent of succinonitrile.

If a tertiary hydroperoxide is decomposed with alkali in the presence of an easily oxidized alcohol like isopropanol or benzhydrol, two competitive reactions take place involving the ROO^- anion: firstly the reaction in which oxygen is produced, and secondly the oxidation of the alcohol diluent by ROO^- (66).

$$\begin{aligned} &C_6H_5(CH_3)_2COO^- + C_6H_5(CH_3)_2COOH \\ &\qquad \longrightarrow C_6H_5(CH_3)_2CO^- + C_6H_5(CH_3)_2COH + O_2 \qquad \text{(cvi} \end{aligned}$$

$$\begin{aligned} &C_6H_5(CH_3)_2COO^- + CH_3CHOHCH_3 \\ &\qquad \longrightarrow C_6H_5(CH_3)_2CO^- + \underset{\displaystyle CH_3COCH_3 + H_2O}{\underset{\downarrow}{\left[CH_3C(OH)_2CH_3\right]}} \qquad \text{(cvii)} \end{aligned}$$

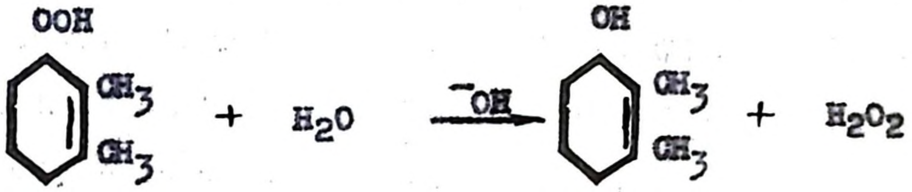
The latter reaction normally does not take place unless the temperature is raised, but can be accelerated by the already mentioned "additives", with the result that oxygen evolution entirely ceases at room temperature.

Reactions (cvi) and (cvii) are then competitive under these conditions. Oxygen is directly transferred ("oxygenation") from the ROO^- anion to the reducing component of the system, i.e., alcohol or hydroperoxide. The amount of oxygen produced then depends on the relative reducing power of the alcohol compared with that of the hydroperoxide, and on the relative concentration of these two reactants.

From the secondary hydroperoxide, cyclohexenyl hydroperoxide, Hock (55), and later Farmer and Sundralingham (75) obtained cyclohexen-3-ol and hydrogen peroxide by heating with warm alkali. The latter workers obtained an 80 per cent yield of the alcohol. They also obtained the corresponding alcohols from 1-methylcyclohexenyl-6-hydroperoxide and 1,2-dimethylcyclohexenyl-3-hydroperoxide.

(cviii)

(cix)



(cx)

In each case, other products were obtained, particularly at higher temperatures. This may be attributed to the reactions of •OH radicals from H_2O_2, or •OH and RO• radicals from the thermal decomposition of the hydroperoxide.

From the primary hydroperoxide of p-xylene, Hock and Lang (11) obtained by decomposition in dilute alkali, p-tolualdehyde. Prolonged heating in excess alkali resulted in production of p-tolylcarbinol and p-toluic acid. They pointed out that the latter products likely were formed by a Canizzarro reaction.

$$2\ p\text{-}CH_3C_6H_4CHO + NaOH \longrightarrow p\text{-}CH_3C_6H_4CH_2OH + p\text{-}CH_3C_6H_4COONa \qquad (cxi)$$

These workers did not, however, indicate a mechanism for the formation of tolualdehyde under the mild conditions. One might consider as a possibility the production of primary alcohol and hydrogen peroxide as per equations (cviii), (cix), and (cx), followed by oxidative interaction of these two products.

$$p\text{-}CH_3C_6H_4CH_2OOH + H_2O \xrightarrow{^-OH} p\text{-}CH_3C_6H_4CH_2OH + H_2O_2 \qquad (cxii)$$

$$p\text{-}CH_3C_6H_4CH_2OH + H_2O_2 \longrightarrow p\text{-}CH_3C_6H_4CHO + 2\ H_2O \qquad (cxiii)$$

A more interesting possibility, however, is a mechanism similar to Kharasch's "oxygenation" of tertiary hydroperoxides (equations (cv), (cvi), and (cvii)).

$$p\text{-}CH_3C_6H_4CH_2OOH + {}^-OH \longrightarrow p\text{-}CH_3C_6H_4CH_2OO^- + H_2O \qquad (cxiv)$$

$$p\text{-}CH_3C_6H_4CH_2OO^- + p\text{-}CH_3C_6H_4CH_2OOH \longrightarrow p\text{-}CH_3C_6H_4CH_2O^- + p\text{-}CH_3C_6H_4CH_2OH + O_2 \qquad (cxv)$$

$$p\text{-}CH_3C_6H_4CH_2OO^- + p\text{-}CH_3C_6H_4CH_2OH \longrightarrow p\text{-}CH_3C_6H_4CH_2O^- + p\text{-}CH_3C_6H_4CHO + H_2O \quad \text{(cxvi)}$$

Kharasch has postulated that whereas no oxygen has been reported as a product of alkaline decomposition of primary and secondary hydroperoxides, the mechanism is applicable only to tertiary hydroperoxides. The possibility remains, however, that oxygen is produced, yet has heretofore been undetected, or that oxygen is produced only to be removed by another reaction. For example, p-tolualdehyde is easily oxidizable, as is p-methylbenzyl alcohol. The ease of oxidation of the latter as compared to tertiary alcohols, makes (cxvi) much more competitive with (cxv) than is (cvii) with (cvi) in the case of cumene hydroperoxide.

An investigation has been carried out in this laboratory by Serif (82) on the autoxidation of p-cymene by two techniques: photochemical, and an aqueous emulsion method in the presence of sodium carbonate. In each case it was demonstrated that both primary and tertiary hydroperoxides are intermediates. An analysis of products further indicated that the "oxygenation" mechanism is fully in accord with the decomposition of the primary hydroperoxide, $(CH_3)_2CHC_6H_4CH_2OOH$, as well as the tertiary hydroperoxide, $CH_3C_6H_4(CH_3)_2COOH$. Further discussion on this work will be given presently.

It is important before proceeding to Metal-Ion Catalyzed Decomposition, to note that certain metallo-organic compounds, for example, cobalt naphthenate, cobalt 2-ethylhaxanoate, iron phthalocyanine, and cuprous cyanide, can catalyze the ionic decomposition of tertiary hydroperoxides into oxygen and carbinol. The rates of these reactions are increased severalfold by traces of alkali. Furthermore, in acetic acid solution, α-cumyl hydroperoxide is decomposed by catalytic amounts of inorganic "additives" like manganese dioxide, chromic oxide, and vanadous chloride. Products are in part oxygen and α-cumyl alcohol, in part oxidation products of α-cumyl alcohol (66).

Metal-Ion Catalyzed Decomposition

The action of metal-ion catalysts in hydrocarbon autoxidation has already been mentioned in connection with Hydroperoxide Formation. Before elaborating on the overall role that such catalysts play, it is well to review again the following points:

(a) George (23) noted that the oxidation rate for tetralin is independent of the catalyst concentration above a certain value.

(b) It was found that the kinetics of the benzoyl peroxide-catalyzed oxidation and the metal-catalyzed oxidation of tetralin were similar. The former has clearly a free radical mechanism; therefore the latter probably has also (21).

(c) Robertson and Waters(28) concluded that the catalyst causes decomposition of the hydroperoxide formed by thermal oxidation into free radicals, which then initiated new chains.

(d) Bawn (71) concurred, and offered a reaction mechanism:

$$Co^{+2} + ROOH \longrightarrow Co^{+3} + RO\cdot + {}^{-}OH \quad \text{or} \quad RO^{-} + \cdot OH \qquad \text{(xi)}$$

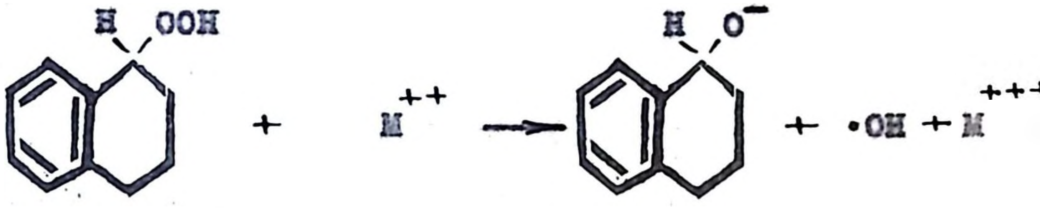
$$Co^{+3} + ROOH \longrightarrow ROO\cdot + Co^{+2} + H^{+} \qquad \text{(xii)}$$

$$ROO\cdot + RH \longrightarrow ROOH + R\cdot \qquad \text{(xiii)}$$

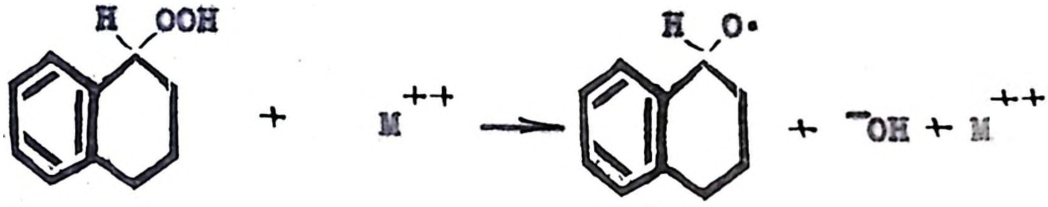
$$R\cdot + O_2 \longrightarrow ROO\cdot \qquad \text{(xiv)}$$

$$ROO\cdot + ROO\cdot \longrightarrow \text{inert products} \qquad \text{(xv)}$$

The decomposition of hydroperoxides by metal-ion catalysts is indeed free radical-producing. Robertson and Waters (27) postulated for tetralin:



(cxvii)



(cxviii)

Bawn's equation (xi) is similar, and offers the same choice.

Robertson and Waters stated a preference for equation (cxvii) rather than for (cxviii). They believed that •OH radicals were produced rather than RO• radicals since the oxidation products were more easily explained in this way.

Kharasch (65), however, has demonstrated unequivocally that RO• radicals are formed in the catalytic decomposition of cumene hydroperoxide. He successfully reacted α-cumyloxy radicals with 1,3-butadiene, isolated the products, and identified them.

$$C_6H_5(CH_3)_2COOH + Fe^{++} \longrightarrow C_6H_5(CH_3)_2CO\cdot + FeOH^{++} \qquad \text{(cxix)}$$

$$C_6H_5(CH_3)_2CO\cdot + CH_2{=}CHCH{=}CH_2 \longrightarrow C_6H_5(CH_3)_2CO\dot{C}_4H_6 \qquad \text{(cxx)}$$

$$2\ C_6H_5(CH_3)_2CO\dot{C}_4H_6 \longrightarrow \text{two isomeric products} \qquad \text{(cxxi)}$$

The primary reaction in hydroperoxide decomposition with metal cations must therefore be accepted as

$$ROOH + M^{++} \longrightarrow RO\cdot + M^{+++} + {}^{-}OH \qquad \text{(cxxii)}$$

although Kharasch prefers to show the ionic product as MOH^{++}, for example, $FeOH^{++}$ in equation (cxix).

Kharasch (41) has studied the free radical decompositions of several hydroperoxides with ferrous ions, and the mechanisms proposed to explain his results are discussed below.

<u>α-Cumyl hydroperoxide</u>: When an aqueous solution of ferrous ammonium sulphate was added to a water suspension of

α-cumyl hydroperoxide and stirred, the following products were obtained:

$$C_6H_5(CH_3)_2COOH \text{ (1 mole)} \xrightarrow{Fe^{++} \text{ (0.47 mole)}}$$
$$C_6H_5COCH_3 \text{ (71\%)} + CH_3OH \text{ (44\%)} + \text{gas (15\%)}$$
$$+ C_6H_5(CH_3)_2COH \text{ (12\%)} + \text{oil (10\%)} \qquad \text{(cxxiii)}$$

(The gas, 73 per cent ethane, 23 per cent methane, accounted for 26 per cent of the hydroperoxide.)

The mechanism proposed by Kharasch includes equation (cxix) as its first step, i.e., the one-electron reduction of the hydroperoxide to RO· radical. However, the RO· radical may undergo a multitude of reactions depending on conditions.

$$C_6H_5(CH_3)_2CO\cdot \xrightarrow{Fe^{++}} C_6H_5(CH_3)_2COH \qquad \text{(cxxiv)}$$

$$C_6H_5(CH_3)_2CO\cdot + C_6H_5(CH_3)_2CO\cdot$$
$$\longrightarrow 2\ C_6H_5COCH_3 + C_2H_6 \qquad \text{(cxxv)}$$

$$C_6H_5(CH_3)_2CO\cdot + C_6H_5(CH_3)_2COOH$$
$$\longrightarrow C_6H_5COCH_3 + CH_3OH + C_6H_5(CH_3)_2CO\cdot \qquad \text{(cxxvi)}$$

$$C_6H_5(CH_3)_2CO\cdot + C_6H_5(CH_3)_2COOH$$
$$\longrightarrow 2\ C_6H_5COCH_3 + C_2H_6 + \cdot OH \qquad \text{(cxxvii)}$$

$$C_6H_5(CH_3)_2CO\cdot \longrightarrow CH_3\cdot + C_6H_5COCH_3 \qquad \text{(cxxviii)}$$

$$CH_3\cdot + C_6H_5(CH_3)_2CO\cdot \longrightarrow C_2H_6 + C_6H_5COCH_3 \qquad \text{(cxxviii a)}$$
$$CH_3\cdot + C_6H_5(CH_3)_2COOH \longrightarrow CH_3OH + C_6H_5(CH_3)_2CO\cdot \qquad \text{(b)}$$

$$C_6H_5(CH_3)_2CO\cdot \longrightarrow C_6H_5(CH_3)\dot{C}OCH_3 \qquad \text{(cxxix)}$$

$$C_6H_5(CH_3)\dot{C}OCH_3 + C_6H_5(CH_3)_2COOH$$
$$\longrightarrow C_6H_5COCH_3 + CH_3OH + C_6H_5(CH_3)_2CO\cdot \qquad \text{(cxxix a)}$$

$$C_6H_5(CH_3)\dot{C}OCH_3 + FeOH^{++}$$
$$\longrightarrow C_6H_5COCH_3 + CH_3OH + Fe^{++} \qquad \text{(b)}$$

The author points out that the major reaction products are accounted for by equations (cxxiv) and (cxxv) which are chain terminating, and (cxxvi) and (cxxix), (a) and (b), which are chain sustaining and lead to methanol and acetophenone. Equation (cxxviii) plays a minor part. Instead, methane arises from the interaction of RO· radicals and some hydrogen donor which may be a reaction product. This latter view is supported by the results obtained when the hydroperoxide was decomposed in a similar manner, but in the presence of a hydrogen donor, DH. Under these conditions the reactions were A and B rather than (cxxv), (cxxvi), (cxxvii), (cxxviii), and (cxxix).

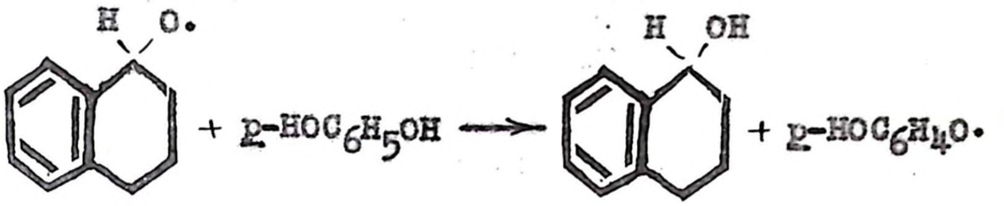
$$C_6H_5(CH_3)_2CO\cdot + DH \begin{array}{l} \xrightarrow{A} C_6H_5(CH_3)_2COH + D\cdot \\ \xrightarrow{B} C_6H_5COCH_3 + CH_4 + D\cdot \end{array} \qquad \text{(cxxx)}$$

It was shown, for example, that in the presence of hydroquinone, carbinol was formed exclusively, yet when the donor was poor, like dextrose, reaction B became increasingly important.

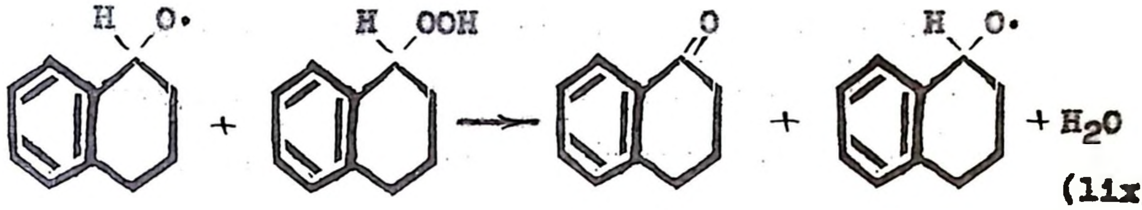
The methane/ethane ratio was found to depend on the concentration of hydroperoxide in water. In the presence of a hydrogen donor and considerable heptane, the concentration of hydroperoxide, and hence RO· radicals in water, is low. The free radicals react preferentially with the hydrogen donor and produce methane. But in the presence of less heptane the concentration of RO· in water is greater, and there is a greater tendency for two RO· radicals to react as in equation (cxxv), with attendant production of ethane.

<u>α-Tetralyl hydroperoxide:</u> Cook (19) reported that iron phthalocyanine catalyzed the decomposition of tetralin hydroperoxide to give largely the ketone. George, Rideal, and Robertson (70) found that both iron phthalocyanine and copper stearate catalyzed hydroperoxide decomposition largely to the ketone. Kharasch (41) found that, although cumene hydroperoxide could be decomposed in the presence of a strong hydrogen donor like hydroquinone to give a quantitative yield of carbinol, tetralin hydroperoxide under the same conditions still yielded appreciable amounts of α-tetralone as well as α-tetralol. The explanation given was that in the latter case an active hydrogen acceptor must also be present, and that this was tetralin hydroperoxide. The following equations illustrate.

$$C_6H_5(CH_3)_2CO\cdot + p\text{-}HOC_6H_4OH \longrightarrow C_6H_5(CH_3)_2COH + p\text{-}HOC_6H_4O\cdot \qquad \text{(cxxxi)}$$



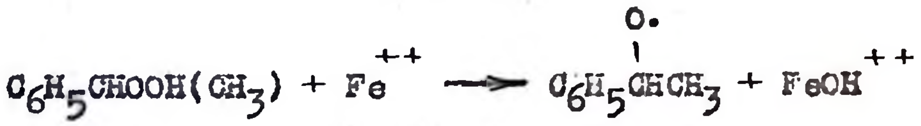
(cxxxii)



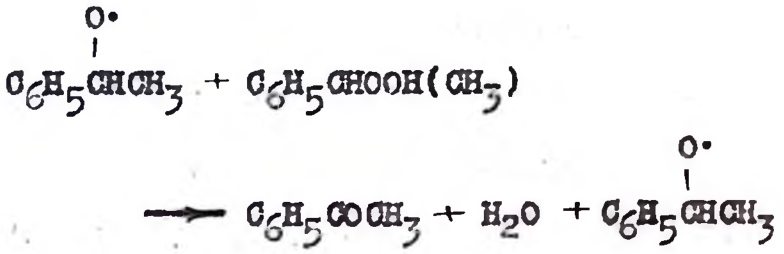
(lix)

The difference is obviously one of structure, the α-tetralyloxy radical having an extra hydrogen which the α-cumyloxy has not.

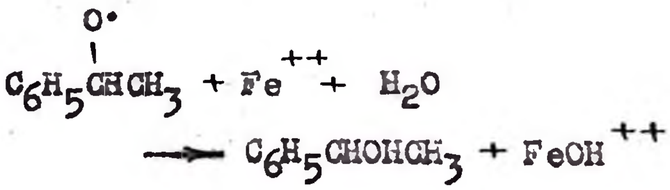
α-Phenylethyl hydroperoxide: Decomposition of α-phenylethyl hydroperoxide in the presence of ten mole per cent ferrous ion has been reported by Kharasch (41). The chain reaction suggested is as follows:



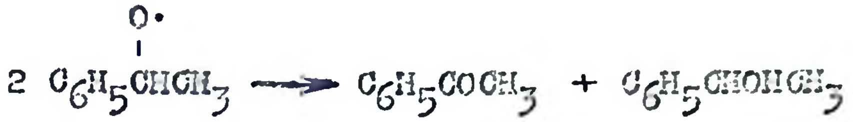
$$C_6H_5CHOOH(CH_3) + Fe^{++} \longrightarrow C_6H_5\overset{O\cdot}{C}HCH_3 + FeOH^{++} \quad (cxxxiii)$$



$$C_6H_5\overset{O\cdot}{C}HCH_3 + C_6H_5CHOOH(CH_3) \longrightarrow C_6H_5COCH_3 + H_2O + C_6H_5\overset{O\cdot}{C}HCH_3 \quad (cxxxiv)$$



$$C_6H_5\overset{O\cdot}{C}HCH_3 + Fe^{++} + H_2O \longrightarrow C_6H_5CHOHCH_3 + FeOH^{++} \quad (cxxxv)$$



$$2\ C_6H_5\overset{O\cdot}{C}HCH_3 \longrightarrow C_6H_5COCH_3 + C_6H_5CHOHCH_3 \qquad \text{(cxxxvi)}$$

The autoxidation of ethylbenzene at 140° C. in the presence of chromium oxide has already been discussed in connection with Thermal Decomposition into Free Radicals (29). In addition to the reactions mentioned in that discussion, some of the above may also have been operative in the oxidation mixture. Equation (cxxxvi) is a particularly intriguing possibility that was not considered by Emerson for ethylbenzene nor by Robertson and Waters for tetralin.

Metal Ions as Oxidants: It has been mentioned previously that oxygen has been reported as a product in thermal decompositions of α-cumyl, α-tetralyl, and tert-butyl hydroperoxides. Basic action of carbinols has been assigned as a likely mechanism. It has also been noted that tertiary hydroperoxides can be decomposed in the presence of alkali to give the corresponding carbinols plus oxygen. In metal-ion catalyzed decomposition, oxygen can also be produced by a mechanism involving free radicals when the metal ions are strong oxidants, for example, cobaltic ions.

Kharasch (66) has studied the decomposition of cumene hydroperoxide with a variety of oxidants, e.g., permanganate, dichromate, ceric sulphate, cobaltous acetate. The first three of these give about one equivalent of oxygen based on the amount of oxidizing agent used. But cobalt acetate decomposes hydroperoxide by a chain reaction and needs be present only in small amounts. The reaction scheme suggested is as follows:

$$C_6H_5(CH_3)_2COOH + Co^{++} \longrightarrow C_6H_5(CH_3)_2CO\cdot + {}^{-}OH + Co^{+++} \qquad \text{(cxxxvii)}$$

$$C_6H_5(CH_3)_2COOH + Co^{+++} \longrightarrow C_6H_5(CH_3)_2COO\cdot + H^{+} + Co^{++} \qquad \text{(cxxxviii)}$$

$$C_6H_5(CH_3)_2CO\cdot + Co^{++} \longrightarrow C_6H_5(CH_3)_2CO^{-} + Co^{+++} \qquad \text{(cxxxix)}$$

$$C_6H_5(CH_3)_2CO\cdot + C_6H_5(CH_3)_2COOH \longrightarrow C_6H_5COCH_3 + CH_3OH + C_6H_5(CH_3)_2CO\cdot \qquad \text{(cxl)}$$

$$C_6H_5(CH_3)_2COO\cdot + Co^{+++} \longrightarrow \left[C_6H_5(CH_3)_2C\right]^{+} + O_2 + Co^{++} \qquad \text{(cxli)}$$

Reactions (cxxxvii), (cxxxix), and (cxl) are the same essentially as (cxix), (cxxiv), and (cxxvi), respectively, presented in the discussion of ferrous catalyzed decomposition of hydroperoxide. But reactions (cxxxviii) and (cxli) are different. The hydroperoxide is <u>oxidized</u> rather than reduced, and oxygen is a product.

The production of ROO· radicals in the decomposition of tertiary hydroperoxides by traces of cobalt salts was subsequently proven by Kharasch (67). Tert-butyl hydroperoxide was decomposed by cobalt acetate or naphthenate in the presence of certain olefins, and reaction products isolated were proven to be adducts of ROO· radicals and the olefins. Evolution of oxygen was suppressed.

Robertson and Waters (27) decomposed tetralin hydroperoxide in the presence of cobalt naphthenate. The ketone/carbinol ratio in the product was the same as in the uncatalyzed decomposition, but the evolved oxygen was nearly equivalent to the carbinol. A reaction mechanism similar to that just shown for cumene was perhaps operative. On the other hand, keeping in mind that ionic reactions such as those mentioned under Base-Catalyzed Decomposition can be catalyzed by cobalt naphthenate and similar additives, the nature of the mechanism is in doubt.

Clearly,the possible mechanisms when soluble organic salts like cobalt naphthenate are used are many. Even moreso is this true when the reaction carried out is the oxidation of a hydrocarbon rather than the decomposition of a hydroperoxide.

Furthermore, examination of a reaction mechanism such as is described by equations (cxxxvii) to (cxli), shows clearly how a small amount of catalyst is able to exert such a great influence. Ions such as cobalt ions do both initiate and terminate chains as early workers postulated. Cobaltous ions are converted to cobaltic and back again so rapidly that an increase in catalyst concentration above a certain value has no further effect.

Products from p-Cymene Oxidation

In addition to the detailed studies on hydrocarbon autoxidation and hydroperoxide decomposition already discussed, there are many references to catalytic oxidation studies that are more practical and commercial in their point of view. Several of these are patents.

King, Swann, and Keyes (31) oxidized ethylbenzene at 100°C. in the presence of a manganese acetate catalyst and obtained better yields of acetophenone than with straight thermal oxidation.

Binapfl and Krey (32) patented a process for the catalytic oxidation of ethylbenzene or cumene at moderate temperatures. A mixture of acetophenone (70-80 per cent) and methylphenylcarbinol (30-20 per cent) was obtained from ethylbenzene, and acetophenone (70-80 per cent) and dimethylphenylcarbinol (30-20 per cent) from cumene.

Loder (33) obtained a patent for the production of benzoic acid and acetophenone from ethylbenzene by metal-catalyzed oxidation at a high temperature in an aliphatic organic acid solvent, e.g., acetic acid. Included also was the conversion of cumene to benzoic acid and tar in the presence of cobalt acetate, but no solvent.

Emerson and Heyd (34) were issued a patent on a process for oxidation of ethylbenzene and cumene at moderate temperatures in the presence of cobalt carbonate and the oxides of other metals. In each case there was obtained a mixture of the corresponding ketone and carbinol containing a larger proportion of the ketone. Two other patents were issued later, one to Emerson and Lucas (35) on ethylbenzene oxidation, and the other to Emerson and Heyd (44) on cumene oxidation. The former, which has been previously mentioned, concerned the production of acetophenone, and the return of by-product carbinol to the next batch. The latter patent concerned the oxidation of cumene at 130-140° C. in the presence of certain oxides and hydroxides, of which calcium hydroxide was the best. A mixture of acetophenone and dimethylphenylcarbinol was obtained containing 59 per cent of the latter.

Senseman and Stubbs (51) studied the oxidation of *p*-cymene at 140-160° C. in the presence of manganese dioxide. The chief products were *p*-toluic acid and *p*-methylacetophenone. In addition, some formaldehyde, formic acid, and terephthalic acid (with prolonged heating) were obtained, as well as carbon dioxide and water.

Palmer and Bibb (47, 48) patented processes involving oxidation of *p*-cymene at 35-50° C. in the presence of special catalysts. The products were cumic acid (obtained in 40 per cent yield based on converted *p*-cymene), and a *p*-methylacetophenone, dimethyl-*p*-tolylcarbinol mixture containing 60-90 per cent of the carbinol.

Cumic acid and dimethyl-*p*-tolylcarbinol from *p*-cymene oxidation have also been reported in a Swedish patent (52). The catalyst was cobalt or manganese cuminate, or finely divided potassium permanganate. Reaction temperature was considerably higher than that specified in the Palmer and

Bibb patents. In fact, 125-160 °C. was recommended for the start-up, and 60-125 °C. thereafter. Yields of cumic acid were 35 per cent, based on converted p-cymene, and the carbinol was produced in up to 60 per cent yield, a higher temperature giving best results.

The Lorand and Reese (Hercules Powder Co.) patents (78, 79) on cumene and cymene oxidation have been mentioned under Base-Catalyzed Decomposition. Oxidation was carried out in the presence of aqueous alkali. The major product, in each case, was the carbinol. From p-cymene, 9-10 per cent cumic acid was obtained as well.

It is important to note that these various p-cymene oxidations yield products most of which have resulted from oxidation of one side chain only. In addition, more often than not, a product mixture contains compounds resulting from oxidation of the "methyl", and other products from oxidation of the "isopropyl". Where the "methyl" remains unchanged, principal products reported are dimethyl-p-tolylcarbinol, p-methylacetophenone, and p-toluic acid. The hydroperoxide intermediate $p\text{-}CH_3C_6H_4(CH_3)_2COOH$ is a stable compound, and can be isolated.

In those molecules with an unchanged "isopropyl", the methyl normally goes to carboxyl (cumic acid). The aldehyde intermediate has been reported as well, however; for example, some Japanese workers (83) obtained cuminaldehyde by oxidation of p-cymene in acetic acid with 30 per cent hydrogen preoxide in the presence of ferrous sulphate. Stephens (14) obtained it by light-catalyzed autoxidation, but it was a minor product.

Helberger, Rebay, and Fetback (84) treated p-cymene with oxygen and sunlight for ten days at 60 °C., and obtained a peroxidic product by alkaline extraction of the reaction mixture, followed by hydrolysis of the sodium salt. The water-clear oil that was obtained agreed in composition with $C_{10}H_{14}O_2$. Upon boiling in water or faintly alkaline solution, it yielded cuminaldehyde.

Serif (82), in this laboratory, repeated this work and confirmed the qualitative tests for a primary hydroperoxide noted by Helberger et al. When the total reaction product was reduced with lithium aluminum hydride, however, and subsequently fractionally distilled, the resulting alcohol product consisted of 20 mole per cent primary alcohol (p-isopropylbenzyl alcohol), and 80 mole per cent tertiary alcohol (dimethyl-p-tolylcarbinol). Furthermore, since the amount of total alcohols formed corresponded exactly to that expected on the basis of known hydroperoxide content in the oxidation product, it can be concluded that the hydroperoxide product was a mixture of 20 per cent primary, $p(CH_3)_2CHC_6H_4CH_2OOH$, and 80 per cent tertiary, $p\text{-}CH_3C_6H_4(CH_3)_2COOH$.

The report of Helberger et al on the production of cuminaldehyde from hydroperoxide decomposition is readily explained. Both hydroperoxides decompose in the presence of dilute alkali to give the respective carbinols.

$$\underline{p}\text{-}CH_3C_6H_4(CH_3)_2COO^- + \underset{\text{(or primary hydroperoxide)}}{\underline{p}\text{-}CH_3C_6H_4(CH_3)_2COOH}$$

$$\longrightarrow \underline{p}\text{-}CH_3C_6H_4(CH_3)_2COH + \underline{p}\text{-}CH_3C_6H_4(CH_3)_2CO^- + O_2 \qquad \text{(cxlii)}$$

$$\underline{p}\text{-}(CH_3)_2CHC_6H_4CH_2OO^- + \underset{\text{(or tertiary hydroperoxide)}}{\underline{p}\text{-}(CH_3)_2CHC_6H_4CH_2OOH}$$

$$\longrightarrow \underline{p}\text{-}(CH_3)_2CHC_6H_4CH_2OH + \underline{p}\text{-}(CH_3)_2CHC_6H_4CH_2O^- + O_2 \qquad \text{(cxliii)}$$

Dimethyl-p-tolylcarbinol under these conditions is relatively stable, but the primary carbinol is further oxidized by direct transfer.

$$\underset{\text{(or tertiary peroxy anion)}}{\underline{p}\text{-}(CH_3)_2CHC_6H_4CH_2OO^-} + \underline{p}\text{-}(CH_3)_2CHC_6H_4CH_2OH$$

$$\longrightarrow \underline{p}\text{-}(CH_3)_2CHC_6H_4CHO + \underline{p}\text{-}(CH_3)_2CHC_6H_4CH_2O^- + H_2O \qquad \text{(cxliv)}$$

p-Cymene autoxidation products resulting from attack on *both* methyl and isopropyl groups are more difficult to produce in large quantities and have been less often reported. The most important of these commercially is terephthalic acid, $\underline{p}\text{-}C_6H_4(COOH)_2$, which has been reported by several workers as a minor autoxidation product (51, 52, 53). The preparation of this acid by the oxidation of p-dialkylbenzenes such as p-xylene, p-cymene, and p-diisopropylbenzene has been claimed in a recent Dutch patent (96). It is claimed, for example, that the normal commercial mixture of isomeric xylenes may be oxidized at 115° C. with air in the presence of cobalt linoleate to give a mixture of isomeric toluic acids, which are then fractionally distilled and the para isomer further oxidized to terephthalic acid in an overall yield of 60 per cent. A similar two-step oxidation of p-cymene or p-diisopropylbenzene is reported to furnish the dicarboxylic acid in 40 per cent yield.

Ciamician and Silber (85) reported on the light-catalyzed autoxidation of cymene, from which they isolated by alkaline extraction, and subsequent acidification, an acidic product. By fractional steam distillation this was separated into cumic acid, p-$(CH_3)_2CHC_6H_4COOH$, p-isopropenylbenzoic acid, p-$CH_2{=}C(CH_3)C_6H_4COOH$, and p-(α-hydroxyisopropyl)benzoic acid, p-$(CH_3)_2C(OH)C_6H_4COOH$. The hydroxy-acid was also mentioned in the Swedish patent (52) as a minor product of a metal-catalyzed autoxidation of cymene. Fichter and Meyer (86) obtained by electrolytic oxidation of p-cymene in dilute sulphuric acid, a variety of products including cuminaldehyde, cumic acid, terephthalic acid, and p-acetylbenzoic acid, p-$CH_3COC_6H_4COOH$. The latter reference is perhaps out of place in a discussion of autoxidation, but is included to show that p-acetylbenzoic acid has been obtained from cymene oxidation. Ciamician and Silber (85) also reported an acid having properties indicating this keto-acid, but the amount recovered was too small for positive identification.

In the present work p-cymene was oxidized in the presence of cobalt naphthenate, and the acidic products were isolated and identified. Cumic acid, p-acetylbenzoic acid, and p-(α-hydroxyisopropyl)benzoic acid, all mentioned above, were obtained, together with the hitherto unreported intermediate hydroperoxide, p-(α-hydroperoxyisopropyl)benzoic acid, p-$(CH_3)_2C(OOH)C_6H_4COOH$. Liquid products were not analyzed.

Subsequently, however, Serif (82) studied p-cymene autoxidation by a different method and isolated products in addition to the four acids just mentioned. He used an aqueous emulsion technique adapted from Armstrong, Hall, and Quin (38) in which the medium was slightly alkaline. Products isolated were the four acids together with dimethyl-p-tolylcarbinol, p-methylacetophenone, and p-isopropylbenzyl alcohol. Furthermore, the extent of oxidative attack at the two positions was shown to be 20 per cent at the "methyl", and 80 per cent at the "isopropyl", an identical relationship with that obtained by Serif in the light-catalyzed oxidation (see p.65).

The products obtained are thought to be in complete accord with the Kharasch "oxygenation" interpretation of alkaline decomposition of hydroperoxides, in spite of the fact that Kharasch assigns the mechanism to tertiary hydroperoxides only. Serif proposes that ROO^- anions from <u>both</u> primary and tertiary hydroperoxides may act by oxygen transfer upon undissociated tertiary hydroperoxide to furnish tertiary alcohol, or upon primary hydroperoxide to give primary alcohol (see equations (cxli), (cxlii), and (cxliii)). "The primary alcohol, however, may also serve as a reducing component, and will be converted, in part, to the corresponding aldehyde, cuminaldehyde. This in turn will be further oxidized, probably by oxygen gas being furnished to the system, to give cumic acid. To a minor extent the tertiary alcohol may serve as a reducing component, and as a result, a small amount will be converted to p-methylacetophenone." Some thermal decomposition to free radicals RO• and •OH, particularly in the case of the primary hydroperoxide, is also mentioned as a concurrent decomposition route.

EXPERIMENTAL

General

As pointed out in the INTRODUCTION, the objectives of initiating a study on *p*-cymene autoxidation were two in number. Firstly, the problem has considerable theoretical interest since cymene has two available and dissimilar centers for oxidative attack, and secondly, it was hoped that a preparative method for terephthalic acid could be developed. In view of the latter aim it was decided that the experimental work would be restricted to a study of carboxylic acid products. Additional interest in the acidic products arose from an apparent conflict in the literature concerning the nature of the acids formed by *p*-cymene autoxidation. As already mentioned, one author (51) reported *p*-toluic acid as the main acidic product, while several more recent investigators (47, 48, 52) have indicated that cumic acid is the principal acid obtained. Terephthalic acid has been reported several times (51, 52, 86, 96), but always as a product of extreme reaction conditions, and with the exception of the Dutch patent (96), never as a major constituent. One author (53) reported all three of these acids.

In view of the findings of previous workers, therefore, it was thought likely that a mixture of *p*-toluic acid and cumic acid would be obtained under moderate oxidation conditions. A partition chromatographic method for the separation of these acids was developed by adapting the techniques of Ramsay and Patterson (87), and Marvel and Rands (88). The acid mixtures obtained from the autoxidations in this laboratory, however, did not include p-toluic acid. This particular chromatographic method, therefore, was never applied to the analysis of the unknown mixtures, and it is discussed separately in APPENDIX 1.

In view of the extreme insolubility of terephthalic acid in all solvents, it was thought unnecessary to work out a chromatographic separation of this compound from other expected acid products. At any rate, under the autoxidation conditions used, terephthalic acid was neither isolated from nor indicated in the reaction products.

The autoxidations themselves were carried out by passing purified air into pure hydrocarbon in the presence of small amounts of cobalt naphthenate and p-cymene hydroperoxide. The reaction was studied at three different temperatures, 50, 105, and 160° C., in order to determine the effect of this variable upon the composition of the acidic product.

A mixture of solid carboxylic acids was obtained from the reaction product by alkaline extraction and subsequent acidification of the extract. The main objectives of the experimental work reported in this thesis were to develop a chromatographic method for quantitatively separating the individual components in the acid mixture, and to identify each. For the acidic products isolated from autoxidations carried out at 50 and 105° C., these objectives were attained. The reaction at 160° C., however, resulted in an acidic product of an extremely tarry nature such as to prevent any separation into pure compounds.

Materials

p-Cymene, Eastman Kodak grade, was dried over Drierite and fractionated under reduced pressure in a 35-plate column packed with glass helices. The material boiling at 67° C. (16.5 mm.), n_D^{20} 1.4906 - 1.4909 (literature 1.4909 (89)), was used in the oxidation experiments.

Cobalt naphthenate (Nuodex Cobalt 6%) was obtained through the courtesy of Nuodex Products of Canada Ltd., Leaside, Ontario.

p-Cymene hydroperoxide, 50% in petroleum ether, presumably prepared by autoxidation of p-cymene in the presence of aqueous alkali, was obtained through the kindness of Hercules Powder Co., Wilmington, Delaware. It is possible that this product was a mixture of primary and tertiary hydroperoxides, and therefore it will be referred to simply as p-cymene hydroperoxide.

Silicic acid, Mallinckrodt Analytical Reagent (specially prepared for chromatographic analysis), was used as purchased. Care had to be taken, however, to keep bottles

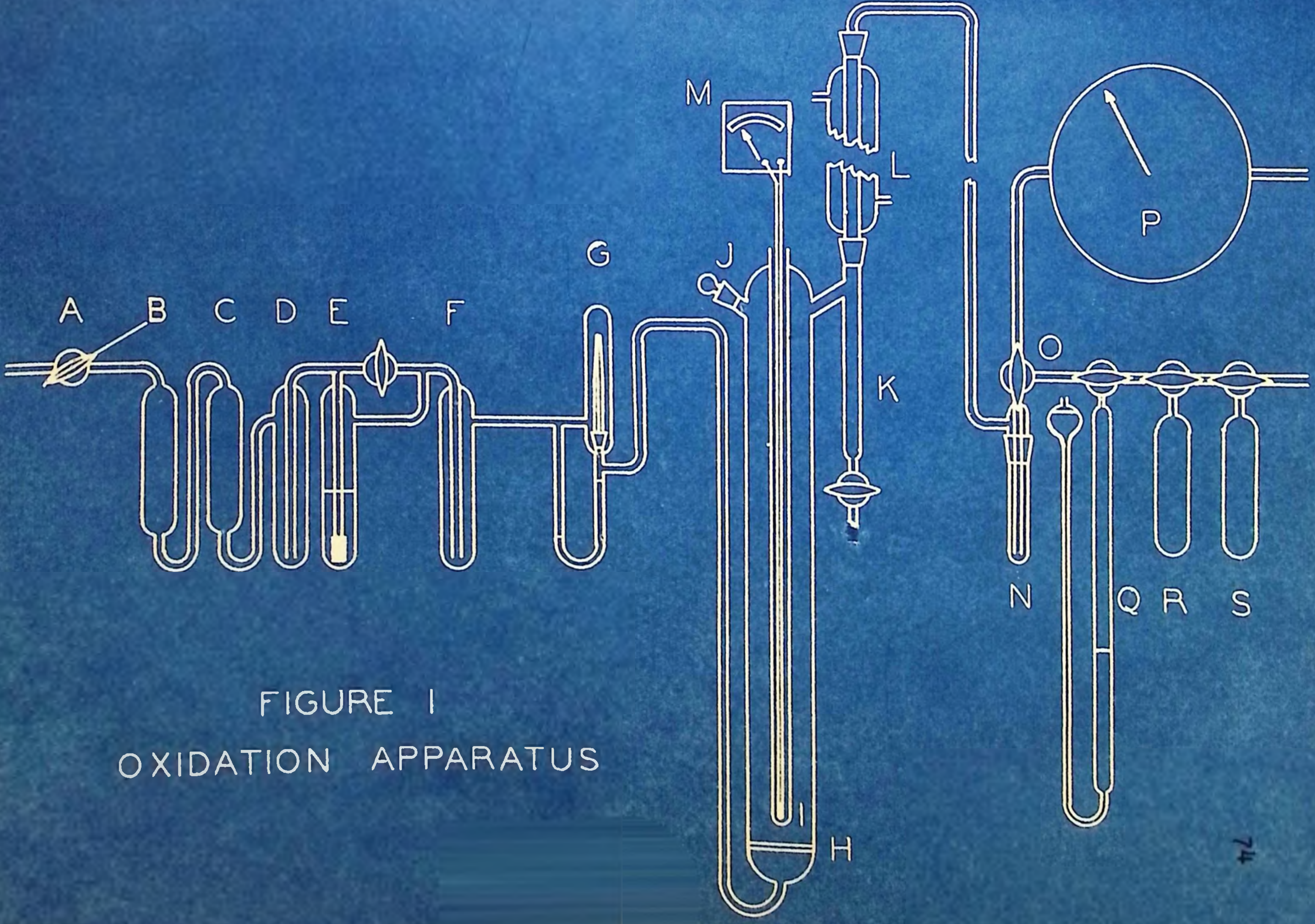


FIGURE I

OXIDATION APPARATUS

tightly stoppered, particularly in humid weather.

Benzene, The Steel Company of Canada, technical grade, was distilled once, and the fraction boiling at 79-81° C. was collected and used in the chromatographic analysis.

Methanol, Dupont synthetic, was used as purchased.

Petroleum ether, Baker and Adamson, boiling range 65-110° C., was distilled once, and the fraction boiling at 65-80° C. was collected and used for chromatographic work. Almost all of the commercial product distilled within this boiling range.

Ether, U.S.P., was distilled once in an all-glass apparatus, and the fraction boiling at 34-35° C. was collected and used in all chromatographic work.

Bromocresol green, British Drug House, was made up as a stock solution, 200 mg. of solid indicator per 25 ml. of methanol.

Oxidation Apparatus

The apparatus used in the oxidations is shown diagrammatically in Figure 1. It consisted of three main parts: the air purification train, the reactor, and the gas analysis apparatus.

Compressed air for the oxidation reaction was passed through a small needle valve, A, to the purification train consisting of a charcoal tower, B, immersed in a dry ice bath, a solid potassium hydroxide tower, C, a back-splash trap, D, a sulphuric acid trap, E, and a Pyrex glass wool tower, F. The gas flow was measured by a mercury differential manometer, G, which was calibrated before use against a wet-test gas meter.

The reaction vessel, constructed of 32 mm. I.D. Pyrex tubing, was fitted at the bottom with a coarse "fritted" glass plate, H, through which the air was introduced. From the top, a 10 mm. O.D. thermocouple well, I, extended concentrically down to within 3 cm. of the "fritted" plate. The top of the reactor was provided with a short addition tube, J, consisting of a standard-taper joint fitted with a glass stopper, and an exit tube leading to a Dean and Stark trap, K, to which was attached a reflux condenser, L. The Dean and Stark trap was included in order that water produced in the reaction would be removed as formed. A chromel-alumel thermocouple was used in conjunction with a Hoskins pyrometer, M.

The distance from the "fritted" plate to the outlet tube was 53 cm., and the effective volume of the reactor was 390 ml.

The reactor was supported vertically on a large carved-out cork in an iron-pipe furnace. The pipe was capped at the bottom, and extended almost to the addition and exit tubes. It was sheathed with asbestos paper, wound with nichrome resistance ribbon (30 ohms), and lagged with corrugated asbestos pipe covering. Wattage was regulated by means of a Variac. Cooling, when necessary, was provided by passing a stream of air into the furnace.

Gases leaving the reactor passed through the water-cooled reflux condenser, and then into a small cold trap, N, immersed in a dry ice-acetone bath. from one arm of a three-way stopcock, O, normal gas flow was to a wet-test gas meter, P, and then to the atmosphere. At frequent intervals, however, a sample of effluent gases was drawn through the other arm of the three-way stopcock into a gas burette, Q. The gas analysis apparatus consisted of the burette, a carbon dioxide absorption pipette, R, containing concentrated potassium hydroxide solution, and an oxygen absorption pipette, S, containing alkaline pyrogallol.

Oxidation Procedure

Each oxidation was carried out using 167.8 g. (1.25 moles) of purified p-cymene. This charge was preheated to approximately twenty degrees below the desired operating temperature in order to easily control the heat of reaction at the beginning of the oxidation. The catalyst (2 ml.of cobalt naphthenate) and the initiator (2 ml. of p-cymene hydroperoxide solution) were added through the addition tube and the air flow was then started.

Oxidations were carried out over a period of some hours during which time frequent temperature and flow rate readings were taken, and analyses made for carbon dioxide and oxygen in the exit gases. The oxygen analyses were taken every few minutes at the beginning until a rapid uptake of oxygen was indicated, and then every hour. In order to take a sample of exit gas for analysis, the gas stream was diverted from the wet-test meter for a short period, an operation which necessitated making a correction each time to the meter reading.

The degree of oxygen utilization in the reaction was followed closely throughout the run by means of the gas analyses. Air is roughly 20 per cent oxygen and 80 per cent nitrogen by volume. At the start-up, then, there was observed a very rapid decline in the oxygen content of the off-gas from 20 per cent to essentially zero. A condition of total oxygen absorption was observed for a period which varied from a few minutes at 50° C. to several hours at the higher temperatures. Then a break in the vigorous reaction occurred as indicated by the presence of oxygen in the exit gases. This change was often a sudden one, the oxygen content rising from zero to 12-14 per cent in one hour. The reaction was continued for several hours until the oxygen content rose to 16-18 per cent at which point the oxidation was terminated. As a rapid but approximate method of checking on the oxygen uptake a comparison of gas rates was also made. For example, the input air rate was identical to the exit rate when no reaction was taking place. On the other hand, an uptake of oxygen in the reaction caused a decrease in the exit gas rate, the maximum decrease being 20 per cent assuming no gases were produced in the oxidation reaction.

Isolation of Reaction Products

On completion of an oxidation the reaction mixture, while still warm, was emptied into a standard-taper flask. The reactor was rinsed with ether, the solvent evaporated on a hot plate, and the residue added to the reaction product. The organic layer in the Dean and Stark trap was also added and the total mixture weighed.

Small amounts of readily volatile materials were present not only in the cold trap, H, but also in the main reaction product. The latter was heated in a water bath at 50° C. and 40-50 mm. pressure, and nitrogen bubbled through the liquid in order to remove the low-boiling components. These were collected in the cold trap. The combined volatile components consisted of an aqueous and an organic layer. These were separated and the former added to the water collected in the Dean and Stark trap during the oxidation reaction. The organic layer was fractionated through a six-inch Podbielniak Heli-Grid column. Fractions collected up to 100° C. proved to be almost entirely petroleum ether, the solvent for the *p*-cymene hydroperoxide used as initiator. The residue from the fractionation was weighed and added to the main product.

As soon as possible after completion of an oxidation the product was analyzed for its hydroperoxide content (see APPENDIX 2). A second hydroperoxide analysis was also made after the removal of the low-boiling compounds under reduced pressure. Hydroperoxides were present in the products of the 50 and 105° C. oxidations only, and no decomposition occurred during the above treatment.

The reaction product was transferred to a separat funnel, the flask was rinsed with a little ether, and the rinsings added to the product. A further quantity of ether, to make a total of 100-150 ml., was then added. (Ether was virtually essential in order to avoid emulsions during the extractions.) The solution was then extracted with small portions (5-20 ml.) of 15 per cent sodium carbonate solution. Each extraction was conducted until vigorous shaking for 30 seconds resulted in no further pressure of carbon dioxide gas. Successive extractions were made until there was little or no precipitate formed when dilute hydrochloric acid was added to the last extract. The total carbonate extract was itself extracted three times with 50 ml. of ether and the ether washings added to the liquid product.

The organic layer from the extraction, hereafter termed the "liquid product", was washed twice with a little water and the washings discarded. It was then dried over Drierite or anhydrous sodium sulphate. The "liquid product" of the oxidation at 50° C. only, after drying, was distilled to remove the ether, and a hydroperoxide determination then made. An appreciable quantity of hydroperoxide was found to be present and it was decomposed by distilling the "liquid product" slowly for three hours with 100 ml. of 8 per cent sodium hydroxide solution. The oils in the distillate and the residue were combined, dried, and fractionally distilled to recover unreacted cymene. The "liquid products" of autoxidation were not further investigated.

The aqueous extract was filtered, and the filtrate placed in a large beaker and cooled in an ice bath. Concentrated hydrochloric acid was then added dropwise with vigorous stirring to liberate the free solid carboxylic acids from their sodium salts. Completion of the reaction was shown by acidity of the mixture to congo red paper. The copious white or brownish solid was filtered with suction, washed with cold water, dried, and weighed. It will hereafter be referred to as the "primary acid product".

The aqueous filtrate from filtration of the "primary acid product" was extracted twice with 50 ml. of ether, or until such time as the final extract yielded no solid on evaporation. The combined extracts were then evaporated leaving a small amount of sticky solid residue. This hereafter will be referred to as the "secondary acid product".

Hydroperoxide determinations were made on both primary and secondary acid mixtures from the oxidation runs at 50 and 105° C. (see APPENDIX 2).

Oxidation Data and Results

After several preliminary oxidation runs a series of three was carried out with the intention of varying temperature only; the operating temperatures for Runs 4, 6, and 7 were 50-53, 105-106, and 160-161° C., respectively. It was found necessary as well, however, to decrease the gas flows with increasing temperature since excessive foaming occurred at lower air rates the higher the operating temperature.

Table I presents the pertinent reaction conditions and results, and Table II gives the material balance for the three runs. The weight of reaction product represents the sum of the organic material in the reactor, in the Dean and Stark trap, and in the cold trap after removal of low-boiling compounds. The volume and weight of oxygen consumed was calculated from exit gas rates and oxygen analyses. The weight of carbon dioxide evolved was similarly calculated from carbon dioxide analyses on effluent gas. Since there were three possible hydroperoxides formed in the oxidation, the two isomeric liquids $p\text{-}CH_3C_6H_4(CH_3)_2COOH$ and $p\text{-}(CH_3)_2CHC_6H_4CH_2OOH$ ($C_{10}H_{14}O_2$), and the solid carboxylic acid $p\text{-}(CH_3)_2C(OOH)C_6H_4COOH$ ($C_{10}H_{12}O_4$), the hydroperoxide analytical figures throughout the table are expressed somewhat differently. Total hydroperoxide content in the reaction product is presented as the percentage by weight of peroxidic oxygen, that is grams of O-O per 100 g. of product. On the other hand, since only $C_{10}H_{14}O_2$ hydroperoxides were considered present in the liquid product, and only $C_{10}H_{12}O_4$ in the acid products, the hydroperoxide contents are expressed as percentage by weight of $C_{10}H_{14}O_2$ and $C_{10}H_{12}O_4$ respectively. The absence of results for Run 7 is due, as already mentioned, to the tarry acidic product which resisted analysis by the chromatographic method. Such information as was available, however, is included for comparative purposes.

Table I

OXIDATION DATA AND RESULTS

Charge: 167.8 g. p-cymene (1.25 moles).

Catalyst: 2 ml. cobalt naphthenate (6 per cent cobalt).

Initiator : 2 ml. p-cymene hydroperoxide (50 per cent).

	Run 4	Run 6	Run 7
Temperature (C.°)	50-53	105-106	160-161
Air rate (ml./min.)	240-250	158-162	81-85
Oxygen rate (ml./min.)	48-50	31-32	16-17
Duration of run (hr.)	18.5	17.2	38.8
Oxygen consumed (liters at NTP)	12.98	16.90	29.10
Oxygen consumed (moles at NTP)	0.579	0.755	1.30
Oxygen consumed (g.)	18.5	24.2	41.6
Reaction product (g.)	190.1	190.2	171.3
Hydroperoxides[a] (%)	1.69	0.030	d
Water produced (g.)	< 1.0	6.9	23.6
CO_2 produced (g.)	0.0	1.2	5.3

Table I (continued)

	Run 4	Run 6	Run 7
Primary acid product (g.)	28.0	20.8	d
Hydroperoxides[b] (%)	14.3	0.0	d
Secondary acid product (g.)	1.3	1.8	d
Hydroperoxides[b] (%)	0.0	0.0	d
Liquid product (g.)	159.7	d	d
Hydroperoxides[c] (%)	5.10	d	d

a. Per cent by weight of O-O.

b. Per cent by weight of $C_{10}H_{12}O_4$.

c. Per cent by weight of $C_{10}H_{14}O_2$.

d. Not determined.

Table II

MATERIAL BALANCE

	Run 4	Run 6	Run 7
Charge (g.)			
p-Cymene	167.8	167.8	167.8
Catalyst and initiator	4.	4.	4.
Oxygen consumed[a]	18.5	24.2	41.6
	190.	196.	213.
Product (g.)			
Main product	190.1	190.2	171.3
Water	<1.	6.9	23.6
Low boilers	0.4	0.2	b
CO_2 evolved[a]	0.0	1.2	5.3
	191.	198.5	200.2

a. Calculated from gas flow rates and gas analyses.

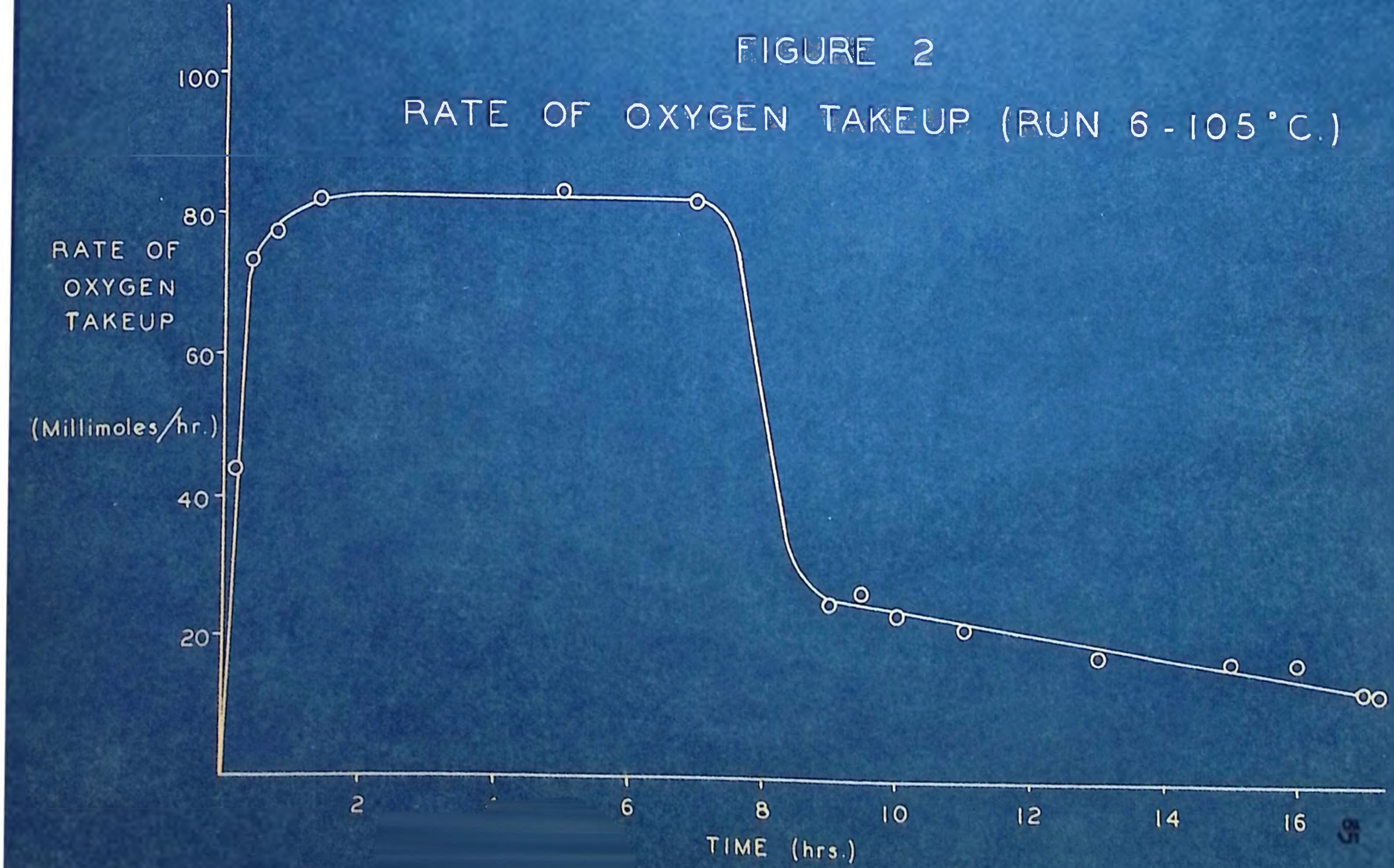
b. Not determined.

Figure 2 is a graph indicating the variations in the rate of oxygen uptake with time for Run 6, the oxidation carried out at 105° C. An initial rapid absorption of oxygen was observed, followed by a period of several hours of almost quantitative oxygen uptake. An extremely sharp decline in the reaction then occurred, followed by a much slower decline. In Run 4, at 50° C., the rapid absorption of oxygen at the beginning was observed, but in a matter of minutes the rate of takeup fell off again rather sharply to half the maximum rate, and then continued to decrease more slowly. In Run 7, at 160° C., the same pattern was followed at the beginning, and then, after about twelve hours of nearly quantitative utilization of the oxygen, a slow decline was observed which continued for another twenty-four hours before dropping suddenly to less than half the maximum rate. None of the reactions were carried to completion, but were stopped when the oxygen content of the exit gases had reached 16-18 per cent.

It should be pointed out that the reaction rates for the three runs cannot properly be compared because air feed rates were different. The plateau displayed in the graph (Figure 2) for Run 6 might have been higher and/or shorter had there been as much available oxygen as in Run 4, or lower and/or longer had there been as little oxygen as in Run 7.

FIGURE 2

RATE OF OXYGEN TAKEUP (RUN 6 - 105 °C.)



Chromatographic Analysis - General

Quantitative separation of mixtures of solid carboxylic acids into component compounds is a problem that, until recently, was very difficult. Older methods such as fractional crystallization and conversion to esters for fractional distillation usually involved considerable losses. Partition chromatography, however, the brilliant development of Martin and Synge (90), for which a Nobel Prize was awarded in 1952, has made older methods virtually obsolete. Originally worked out as an extension of countercurrent liquid-liquid distribution for the separation of acetylated amino-acids, the technique now has wide application in the separation of many types of compounds.[a]

In partition chromatography the substances to be separated are distributed between two liquid phases, one of which is mobile and the other fixed. The latter is adsorbed on a support which may or may not participate in the separation process. The support may be a column of a substance like silicic acid, starch, or cellulose, or it may be a strip or sheet of filter paper. In each case, one fluid is adsorbed and fixed on the support, and another fluid flows over it.

Partition chromatographic separations of some fatty acids worked out by Ramsay and Patterson (87) were later extended by Vandenheuvel and Hayes (92). A group of acids with greater variety of structures was separated by Marvel

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[a] For pertinent references, see Cassidy (91).

and Rands (88). The methods of all these workers were found useful in developing a chromatographic method for analyzing the acid mixtures obtained from p-cymene autoxidations.

As already pointed out, a chromatographic separation was first made on synthetic mixtures of two expected acidic oxidation products, p-toluic and cumic acids. Since toluic acid was not obtained as an oxidation product, however, and since the techniques used differed in some respects from the general method that was subsequently developed for analyzing the unknown acid mixtures, the toluic-cumic separation is described in APPENDIX 1.

In the method found applicable to the separation of the acid products of the oxidation reaction, silicic acid columns were used in which aqueous methanol was the stationary phase. An acid-base indicator, bromocresol green, was mixed with the support in order that the acid bands could be visually observed on the column. Benzene was the mobile phase, or eluent, used in the main separations into constituent acids. In order to obtain pure samples for identification purposes, however, certain fractions had to be rechromatographed in smaller columns, and petroleum ether was in some cases used as the eluent.

All of the partition chromatographic literature consulted emphasized that only extremely small samples of material should be analyzed. amounts of the order of a few milligrams were common. The use of small quantities of solvent for introducing the samples on to the top of the column was likewise reported as important. The writer, however, was anxious to isolate workable quantities of component compounds from the mixtures (one or more grams). Both "rules", therefore, were more or less ignored, and with remarkable success.

In all the separations, the acid bands were eluted and collected separately, and the solid compounds isolated by distillation of the solvent. These were then weighed and identified. The compounds isolated were, in order of elution, cumic acid p-$(CH_3)_2CHC_6H_4COOH$, p-acetylbenzoic acid p-$CH_3COC_6H_4COOH$, p-(α-hydroperoxyisopropyl)benzoic acid p-$(CH_3)_2C(OOH)C_6H_4COOH$, and p-(α-hydroxyisopropyl)benzoic acid p-$(CH_3)_2C(OH)C_6H_4COOH$.

Chromatographic Apparatus

Two tube sizes were used in the chromatographic analysis. A large column, A, used in the main analyses on the "primary acid product", was a four-foot length of 35 mm. O.D. Pyrex glass, with a constriction at one end. A smaller column, B, used in the analyses of the "secondary acid product" and in rechromatographing of fractions obtained in the initial separation of the "primary acid product", was 40cm. in length, 19 mm. O.D. Pyrex glass, constricted at the bottom and fitted with a 200 ml. liquid reservoir at the top.

A diagram of the apparatus is presented as Figure 3.

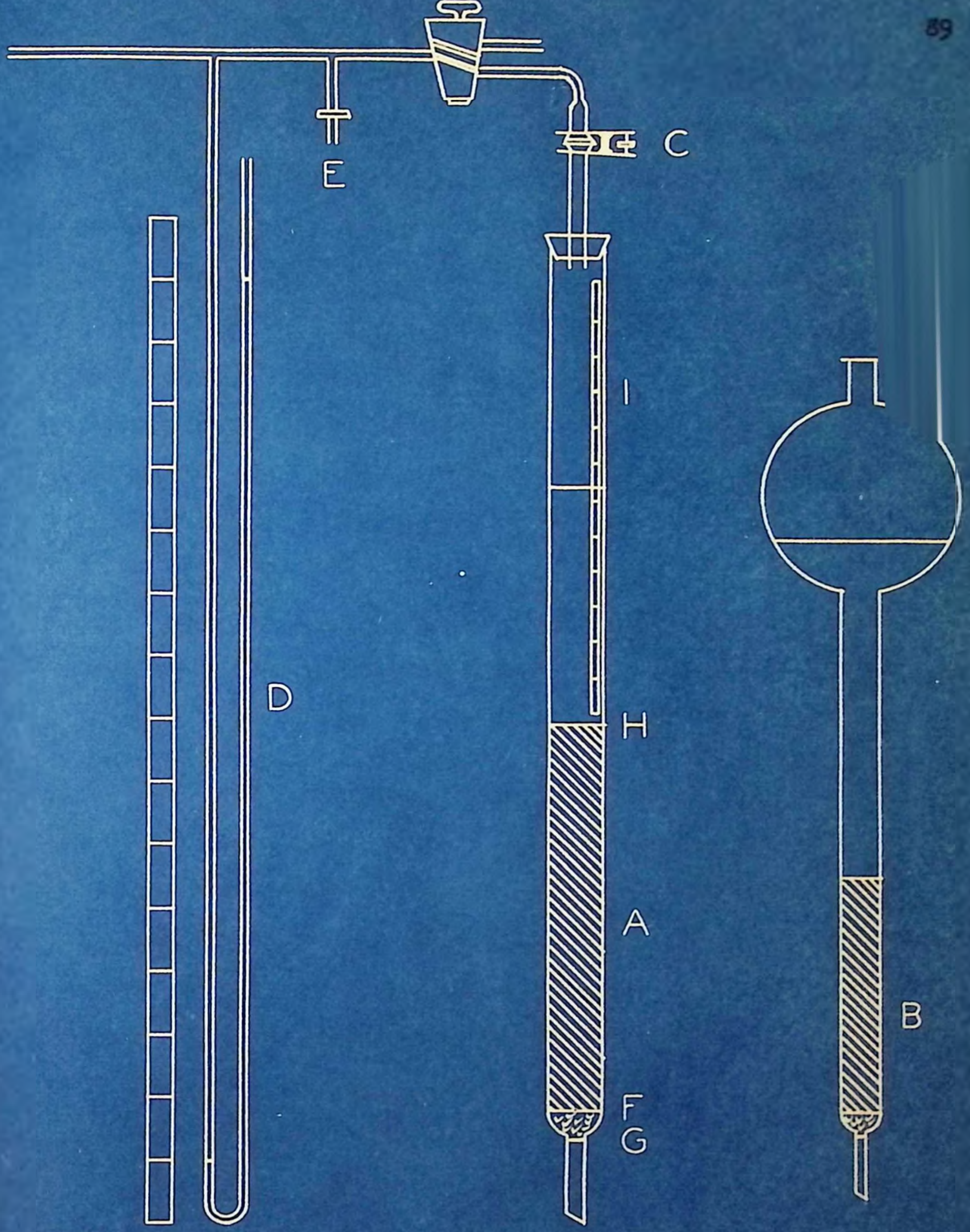

FIGURE 3 CHROMATOGRAPHIC APPARATUS

In both columns pressure was required to force the eluting liquid through the packing. A connection to the laboratory compressed air line was made at the top of the column by means of a spherical joint, C. Pressures of the order of 30 cm. of mercury were used for packing and developing the large columns. The pressure was measured by a mercury manometer, D, and was controlled by means of a variable leak, E. The packing was supported in the column by means of a white blotting paper disk, F, placed on a plug of glass wool, G. A second blotting paper disk, H, was placed on top of the packing.

In order to measure the amount of liquid eluted at any given time, the free space in the tube above the packing was graduated using a paper scale, I.

Preparation of Columns

Before preparing the column mixture, the optimum ratio of methanol to silicic acid was determined using the method suggested by Ramsay and Patterson (37). Five grams of silicic acid and 2.5 ml. of methanol were well mixed by means of a mortar and pestle. Additional methanol was added in 0.5 ml. portions until the mixture was just slightly gummy and sticky. This point was reached after a total of 8 ml. had been added. The proper amount of methanol for a free-flowing powder, rich in stationary phase, was therefore slightly less than 8 ml. of methanol per 5 g. of silicic acid. In preparation of individual columns the amount of methanol was calculated on this basis.

The requisite amounts of methanol and indicator stock solution were measured out and a few drops of 1 N ammonium hydroxide were added. The silicic acid was placed in a mortar, to which the methanolic solution was then added, and the whole thoroughly mixed with a pestle until a powder of a uniform green color was obtained. Good mixing and complete homogeneity were important.

The amounts of the ingredients used, together with the column sizes, and actual packed heights are presented in Table III. Column A was used for the main chromatograms. Columns B_1, B_2, and B_3 were all packed in the small-sized tubes. Columns B_1 and B_2 differ only in that benzene was used in the former as the eluent for the "secondary acid products", and petroleum ether was used in the latter for rechromatographing main fractions. Column B_3 was used for purposes similar to B_2, but the column height was much less.

To the prepared powder was added about 75 ml. of benzene or petroleum ether per 25 g. of silicic acid. A smooth green slurry was formed by mixing with a spatula, and the slurry was then poured into the tube and excess liquid forced out by applying a slight pressure to the system. A uniform column was promoted by tapping the tube during the packing process, and was considered ready for use only when the top of the silicic acid mixture no longer moved downward

Table III

PREPARATION OF CHROMATOGRAPHIC COLUMNS

	A	B_1	B_2	B_3
Inside diameter (mm.)	31	17	17	17
Packed height (cm.)	38	21	21	4
Silicic acid (g.)	150	25	25	5
Methanol (ml.)	195	32	32	6.4
Indicator solution (ml.)	7.5	1.25	1.25	0.25
1 N NH_4OH (drops)	60	10	10	2
Eluting liquid	Benzene	Benzene	Pet. Ether	Pet. Ether

with respect to the tube. As already mentioned, a snugly fitting blotting paper disk was inserted on top of the column mixture without exerting any manual pressure upon the packing[a].

After the mixture was successfully packed in the chromatographic tube, some excess solvent usually remained on top. This was poured off and replaced with fresh aqueous methanol-equilibrated benzene, hereafter called "equilibrated benzene" [b], which was passed through the column under pressure until eluted liquid emerging from the bottom was perfectly clear and free from excess indicator.

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[a] Vandenheuvel and Hayes (92) reported that reproducibility of their columns depended greatly upon this factor.

[b] The eluting liquids, benzene and petroleum ether, were equilibrated before use with 90 per cent aqueous methanol. Two liters of distilled solvent was shaken vigorously with 50 ml. of 90 per cent aqueous methanol, allowed to stand, and the clear solvent decanted or siphoned off.

The slight excess of ammonium hydroxide which was present in the column mixture was neutralized in the following manner: Approximately one-half gram of cumic acid was dissolved in 20 ml. of equilibrated benzene, and the solution placed carefully on top of the packing. This was pushed into the column under pressure, and at the precise moment when the last of the solution had passed into the column the pressure was released. Small additional portions of solvent were used to rinse down the tube, and each was carefully forced into the packing. The tube above the packing was then filled with equilibrated benzene and the cumic acid was forced through the column under pressure. Its passage downward was marked by a yellow band.

Development of Chromatograms

A sample of a crude acid mixture was thoroughly dried by placing in a vacuum desiccator for a few hours. This treatment was particularly useful for the "secondary acid products" which were sticky in nature.

Into a 50 ml. standard taper Erlenmeyer flask was weighed a 1.8-1.9 g. sample of crude acid if a large column was to be used, 0.1 g. for the smaller columns. Thirty ml. of benzene was added to the larger samples and a proportionate amount to smaller ones, and the suspension was heated under reflux for a short period to effect solution.[a] After allowing

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[a] Crude acid mixtures were as a rule more readily

the solution to cool overnight a solid, which proved to be a pure compound, p-(α-hydroxyisopropyl)benzoic acid, crystallized out.

The crystals were filtered, washed with fresh solvent, dried in a vacuum desiccator, and weighed. The filtrate was poured slowly into the prepared column and forced into the packing under a slight pressure. As the level of the liquid approached the surface of the packing, the pressure was quickly released.[b] Both the filter flask and the tube were rinsed with small quantities of solvent and rinsings pushed into the column.[c]

For development of the chromatogram, the tube above the packing was filled with "equilibrated benzene" and pressure applied. The presence of organic acids at any point in the green column was sufficient to bring about a color change

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soluble in small quantities of solvent than were pure individual components. A much larger amount of solvent was necessary to dissolve p-acetylbenzoic acid, for example, than was used to dissolve the same amount of that acid in the presence of other acids.

[b] Failure to release the pressure in time causes drying out of the column, and the air thus introduced results in channeling when more solvent is added. Channeling completely spoils the chromarogram since it causes extremely uneven bands. Furthermore, the addition of more solvent, and application of pressure is seldom effective in removing the air. The best procedure is to discard the packing. If drying out occurs when no sample is present, however, the packing can be extruded, reslurried, and the column repacked.

[c] The introduction of small amounts of material, i.e. up to 100 mg., such as were chromatographed in the smaller columns, was effected by totally dissolving the sample, and then pipetting the solution carefully on to the packing.

of the indicator from green to yellow. Development of the chromatogram, therefore, was visible as a series of yellow bands moving downward against a green field. Colors observed ranged all the way from bright orange to a barely visible lightening of the green. Intensity of color varied directly with acid concentration.

Development of chromatograms resulted in a separation of the primary mixtures into four component acids. Complete elution of 1.8 g. as four fractions from a large column was achieved with about 1.5 liters of solvent. Even bands were required to accomplish good separations. In other words, the visible front of each band had to be reasonably level around the circumference of the tube. Careful packing and insertion of the blotting paper disk helped to ensure this condition.

The first band moved very rapidly. Its rate of travel was not much less, if at all, than the flow of solvent. The second, third, and fourth bands moved much more slowly, but differed sufficiently in rate, one from another, to ensure reasonably good separations. The separation between the third and fourth bands was the poorest. The final compound lingered in the column rather badly, possibly due in part to the absence of the "push" of subsequent bands.

Besides the four major bands, smaller minor bands were also encountered. They represented a small proportion of the total acid mixture and upon isolation, proved to be oily, unidentifiable material. The amount of oily materials, however, increased directly with oxidation temperature, and was so great in the product from the 160° C. oxidation that chromatographic analysis could not properly be carried out.

Figure 4 is a graphical presentation of the progress of a chromatogram.

Isolation of Acids

Eluted solution was collected for acid recovery as soon as the first band neared the bottom of the column. Separations were made visually by changing fractions when the front of a new band was a few millimeters from the bottom of the packing. When a very pure sample of an acid was desired for identification purposes a narrow fraction was collected from the middle of a band.

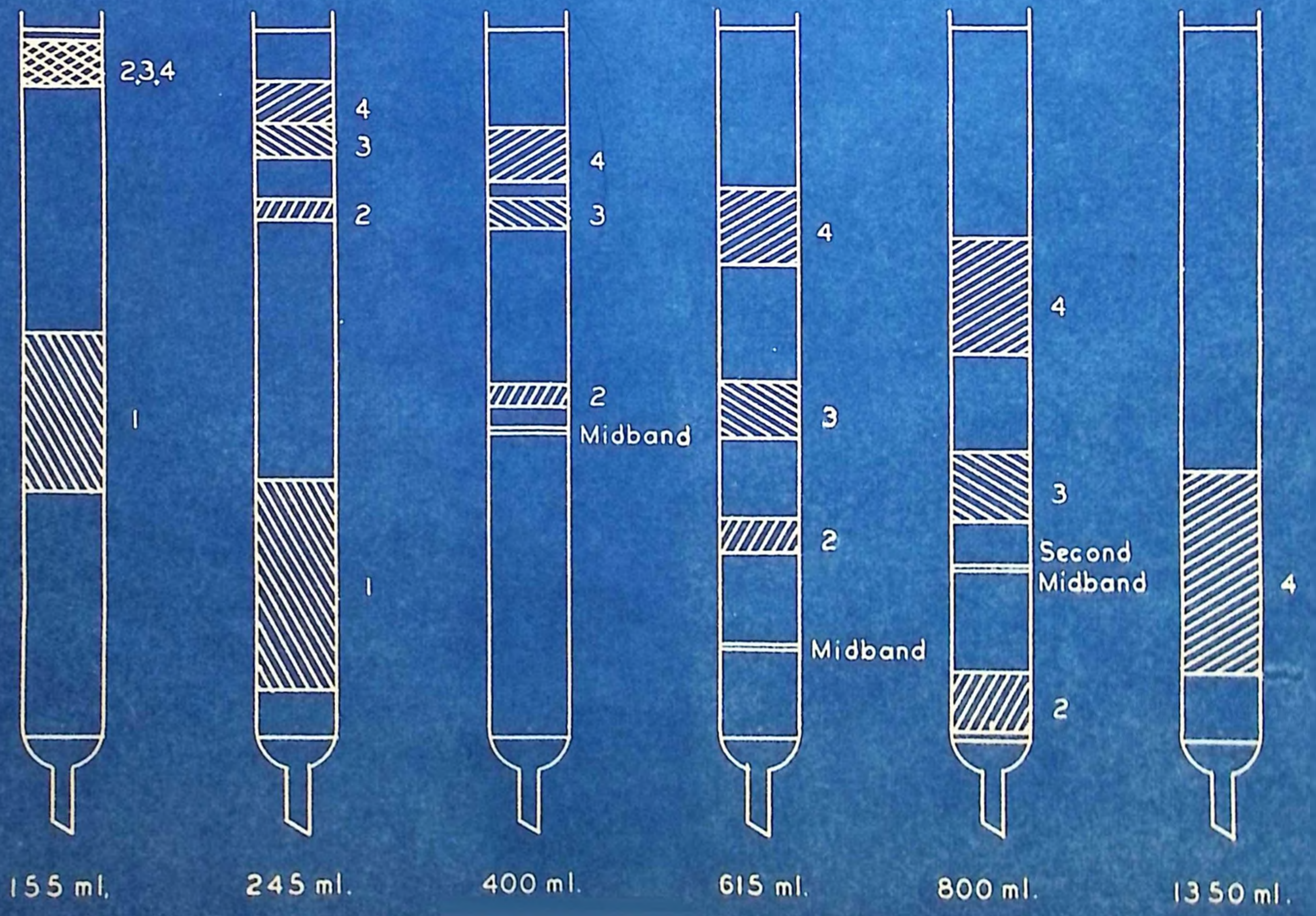
Solvent was removed from the eluted fractions by distillation under reduced pressure from a warm water bath and could be used again in subsequent separations. The solid residues were transferred to tared 30 ml. beakers using ether. The ether was evaporated by slight warming, not boiling, and final traces of solvent were removed in a vacuum desiccator.

Effluent Volumes and "R" Values

In partition chromatography the movement of a band on a column can be expressed as an "R" value, which is related to the distribution coefficient of the compound,

FIGURE 4

A TYPICAL CHROMATOGRAM (C 31)



and serves to characterize the substance (91).

$$\text{"R"} = \frac{\text{Movement of position of maximum solute concentration}}{\text{Simultaneous movement of surface of developing phase in empty part of tube above the partition column}}$$

In the work reported here, positions of maximum concentration of solute were not determined. An approximation for "R" values, however can be made since effluent volumes were noted for each band. That is, the volume of developing phase was recorded for the travel of each band from the top of the column to the point where the front started to pass out of the column (large column only). The volumes reported include the solvent used to introduce the sample on to the column.

The distance travelled by the bands was 39.5 cm. (15.5 in.), and the volume of the free space above the packing was 19.90 ml./in.

The data obtained from several chromatograms are tabulated in Table IV. Two sets are from the analysis of the "primary acid product" from Run 4, and two from the product of Run 6. The "R" values were obviously not very reproducible. However, other workers (91) have found that "R" values display inconsistancies arising from the lack of reproducibility of columns and the variation in sample size and composition. Relative "R" values have been used for identification purposes by some workers (87) since they are usually more constant.

Table IV

EFFLUENT VOLUMES AND "R" VALUES

Effluent Volumes in ml. (A)

Band	"Primary acid product" - Run 4		"Primary acid product" - Run 6	
	Analysis C 23	Analysis C 31	Analysis C 25	Analysis C 32
1	238	252	217	241
2	721	790	580	813
3	943	1095	-	-
4	1168	1440	1045	1383
Travel of Developing Solvent in in. (B=A/19.9)				
1	12.0	12.7	10.9	12.1
2	36.2	39.7	29.1	40.9
3	47.4	55.0	-	-
4	58.6	72.2	52.4	69.6
"R" Values (15.5/B)				
1	1.29	1.22	1.41	1.28
2	0.43	0.39	0.53	0.38
3	0.33	0.28	-	-
4	0.26	0.21	0.29	0.22

Identification of Acids

The following solid carboxylic acids were first considered to be possible components of the acid product of *p*-cymene oxidation: cumic, I, *p*-toluic, II, the keto-acid *p*-acetylbenzoic, III, the hydroxy-acid *p*-(α-hydroxyisopropyl)benzoic, IV, the unsaturated acid *p*-isopropenylbenzoic, V, and the dibasic acid terephthalic, VI.

$p\text{-}(CH_3)_2CHC_6H_4COOH$ I $p\text{-}CH_3C_6H_4COOH$ II

$\underline{p}$-$CH_3COC_6H_4COOH$ III $\underline{p}$-$(CH_3)_2C(OH)C_6H_4COOH$ IV

$\underline{p}$-$CH_2{=}C(CH_3)C_6H_4COOH$ V $\underline{p}$-$HOOCC_6H_4COOH$ VI

It was fairly readily established by the usual procedures that the acids comprising the first, second, and fourth bands were compounds I, III, and IV, respectively. The acid of the third band clearly did not correspond to the remaining compounds, II, V, and VI, nor was there at any time evidence of the presence of any of these compounds in the acid product.[a] After some difficulty this acid was identified as the hydroperoxidic intermediate, p-(α-hydroperoxyisopropyl)-benzoic acid, VII.

$\underline{p}$-$(CH_3)_2C(OOH)C_6H_4COOH$ VII

Acid samples for identification by melting point and neutralization equivalent were purified by repeated recrystallizations. Cumic acid was recrystallized to constant melting point from water-ethanol, and the other acids from benzene-ethanol.

Melting point determinations were made in an oil bath apparatus and the thermometer was calibrated against a set of Anschutz thermometers previously standardized by the National Research Council, Ottawa. All reported values are corrected.

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[a] The question of the absence of p-toluic acid is discussed further in APPENDIX 1.

Neutralization equivalent determinations were successfully carried out on samples of the order of 50 mg. Carefully weighed samples were dissolved in 5 ml. of ethanol and a little water, and were titrated with 0.02 N sodium hydroxide.

The identification data are tabulated in Table V. It will be noted that neutralization equivalent values for p-acetylbenzoic acid were not very good, and for this reason a phenylhydrazone was prepared and its melting point determined.

For the identification of p-(α-hydroperoxyisopropyl)benzoic acid, a new compound, special methods were used. The equivalent weight was determined by analysis for peroxidic oxygen (APPENDIX 2), and the compound was converted to p-(α-hydroxyisopropyl)benzoic acid by reduction with sodium sulphide, and to a mixture of this compound and p-acetylbenzoic acid by catalytic decomposition in the presence of cobalt ion.

<u>Sodium Sulphide Reduction of p-(α-Hydroperoxyisopropyl)benzoic Acid:</u> To a solution of 0.0854 g. of p-(α-hydroperoxyisopropyl)benzoic acid in 0.5 ml. of 10 per cent sodium carbonate and 4.5 ml. of water was added 0.1 g. of sodium sulphide hydrate dissolved in 5 ml. of water. The solution was heated under reflux with stirring overnight. It was then acidified, the precipitated acids taken up in ether and the ether removed by evaporation. The solid residue was dissolved in benzene and chromatographed on a small column, type B_1

Table V

IDENTIFICATION DATA FOR ACID PRODUCTS

	Cumic acid	*p*-Acetyl-benzoic acid	*p*-(α-Hydro-peroxy-isopropyl)-benzoic acid	*p*-(α-Hydroxy-isopropyl)-benzoic acid
Melting Point				
Literature	119° C. (85)	210° C. (93)	-	156-7° C. (94)
Found	118.6-119.0° C.	209.2-209.8° C.	151.5-151.8° C.	159.2-159.6° C.
Neutralization Equivalent				
Calculated	164.20	164.15	196.20	180.20
Found	164.7 ± 0.1	168.3 ± 0.6[a]	196.9	180.5 ± 0.1
Phenylhydrazone M.P.				
Literature	-	234° C. (95)	-	-
Found	-	234.0-234.5° C.	-	-
Equivalent Weight[b]				
Calculated	-	-	196.20	-
Found	-	-	193.6 ± 1.2[c]	-

a. Analyses were determined on different samples for which the individual values were 168.9 and 167.7 .

b. The equivalent weight was calculated from peroxidic oxygen analyses as explained in APPENDIX 2.

c. Analyses were determined on different samples for which the individual values were 192.5, 193.5, and 194.8 .

(see Table III). There was obtained 0.0027 g. of p-acetylbenzoic acid (3.8 per cent yield), and 0.0694 g. of p-(α-hydroxyisopropyl)benzoic acid (88.5 per cent yield).

Cobalt-Ion Catalyzed Decomposition of p-(α-Hydroperoxyisopropyl)benzoic Acid : To a solution of 0.1503 g. of p-(α-hydroperoxyisopropyl)benzoic acid in 45 ml. of benzene was added six drops of cobalt naphthenate catalyst. The solution was heated under reflux overnight. Acidic products were then extracted with 10 per cent sodium carbonate solution, and the extract filtered and acidified with 20 per cent hydrochloric acid. The precipitated acids were taken up in ether and the ether removed by evaporation. The solid residue was dissolved in benzene and chromatographed on a small column, type B_1 (see Table III). There was obtained 0.0465 g. of p-acetylbenzoic acid (36.9 per cent yield) and 0.0590 g. of p-(α-hydroxyisopropyl)benzoic acid (42.7 per cent yield).

Composition of Acid Products and Yields of Component Acids

The results of the chromatographic analyses on th acid mixtures from Runs 4 and 6 are presented in Table VI. The detailed chromatographic data upon which the "composition of acid product" figures are based, are presented in APPENDIX 3.

The percentage yields of the acid components based on converted cymene could only be calculated with assurance for Run 4 since only for this run was the weight of unconverted hydrocarbon determined. A figure for converted cymene can

Table VI

YIELDS OF ACID PRODUCTS

	Composition of Acid Product (% by weight)		Per Cent Yield Based on Converted Cymene		
			Unoxidized cymene recovered	Unoxidized cymene calculated from oxygen consumption[a]	
	Run 4	Run 6	Run 4	Run 4	Run 6
Band 1, cumic acid	44.0	54.9	11.5	10.7	9.35
Midband (oily)	1.7	10.2			
Band 2, *p*-acetylbenzoic acid	4.1	8.0	1.07	0.99	1.36
Midband (oily)	0.3	1.3			
Band 3, *p*-(α-hydroperoxy-isopropyl)benzoic acid	13.3	0.0	2.90	2.70	0.0
Band 4, *p*-(α-hydroxyisopropyl)-benzoic acid	33.8	22.1	8.00	7.48	3.34
Totals	97.2	96.5	23.5	21.9	14.05

[a]. See APPENDIX 4

also be calculated, however, from oxygen consumption data (see APPENDIX 4) provided that the following assumptions are made:

(a) The oily and unidentifiable material in the acid product contained oxygen to the extent of one quarter to one third of its weight. This compares closely to the oxygen content of the isolated oxy-acids.

(b) The hydroperoxide present in the "liquid product" was a mixture of p-$(CH_3)_2CHC_6H_4CH_2OOH$ and p-$(CH_3)_2C(OOH)C_6H_4CH_3$.

(c) The "liquid product" contained besides hydroperoxides and unreacted cymene, only p-methylacetophenone and dimethyl-p-tolylcarbinol, the ketone/carbinol molar ratio being that found when p-(α-hydroperoxyisopropyl)benzoic acid was decomposed with cobalt ion to p-acetylbenzoic acid and p-(α-hydroxyisopropyl)-benzoic acid, namely 0.865 (see p.103).

The yield figures for Run 4 calculated by the two methods show excellent agreement, and this gives confidence to the figures for Run 6 based on oxygen consumption data. The latter results, however, may be poorer for Run 6 than for Run 4 since considerably more oily material was produced at the higher oxidation temperature.

DISCUSSION

The main contribution of the work reported in this thesis has been the development of a detailed procedure for the study of p-cymene oxidation, the development of a partition chromatographic method for the separation of the complex acid product, and, finally, the characterization of the isolated acids, including a new compound, p-(α-hydroperoxyisopropyl)benzoic acid. The chromatographic method has already proved useful in the extension of the p-cymene work in this laboratory by Serif (52), in which an accurate measure of the relative reactivity of the two alkyl side-chains has been determined.

In spite of the rather limited scope of the work, certain significant conclusions can be drawn. The complete absence of p-toluic acid in the product, for example, has been definitely established (APPENDIX 1). In view of previously reported work, particularly that of Senseman and Stubbs (51), this was contrary to expectation. There appears to be no doubt that these workers did obtain p-toluic acid in good yield, for they definitely identified the product by melting point, boiling point, and neutralization equivalent. This disparity between their results and ours must be attributable to a difference in oxidation conditions. A temperature difference alone does not seem to be the likely governing factor, but the catalysts are distinctly not alike. Whereas soluble heavy metal salts have been utilized for the formation of cumic and other acids, but not toluic, both here and in previously reported work (47, 48, 52), Senseman and Stubbs (51) produced p-toluic acid by cymene oxidation in the presence of finely divided manganese dioxide specially prepared to give a large surface. Instead of a free radical chain mechanism such as is obtained with cobalt ions, an entirely different catalytic action may have been involved.

There are several points to note with respect to the data presented in Table VI. An increase in temperature under our oxidation conditions, although increasing the total oxygen uptake, results in a poorer yield of isolable acids and much larger quantities of oily material. The increase in oxygen consumption is largely accounted for not by oil formation, however, but by the production of larger quantities of water and carbon dioxide with increased temperature. These products indicate secondary oxidations of the one-carbon fragments which have split off from the isopropyl groups in ketone formation. This is consistent also with the production of more keto-acid and less hydroxy-acid at the higher temperature. There is no obvious explanation for the decreased yield of total acids with increased temperature, although it may be due to a competition for the limited oxygen available by reactions leading to carbon dioxide and water.

Although the acid product of Run 7 (160° C.) was not analyzed, this oxidation is not without interest. There was an even greater oxygen consumption than for Run 6, a greater production of both water and carbon dioxide, and a very large proportion of oily materials in the acid product.

With respect to a further extension of the work in a search for a preparative method for terephthalic acid from cymene, the results reported give little guidance. Although this acid has been reported as a minor product in previous work using extreme reaction conditions (51, 52, 53), the extension of our method to higher temperatures would certainly result in much loss to oils and tars. The use of pressure or an acidic medium might be more fruitful.

It should be pointed out that in addition to the patents (49, 50) mentioned in the INTRODUCTION, and the Dutch process (96) for a two-step oxidation of dialkylbenzenes (see p. 66), other patents have been issued even more recently for the preparation of terephthalic acid. The catalytic oxidation of p-methylbenzaldehyde in acetic acid solution (97), the aqueous permanganate oxidation of p-methylbenzyl chloride (98), and the oxidative hydrolysis of chloroalkylbenzenes (99), have all been recommended.

Bearing a close relationship to the present study is the two-stage oxidation of p-dialkylbenzenes reported in a very recent California Research Corporation patent (100). Catalytic oxidation of the hydrocarbon to p-toluic acid at 200-400° F. is followed by a non-catalytic oxidation at

400-500 °F. *p*-Xylene is the example cited, and it is interesting to note that while air is used in the first step, oxygen is recommended in the second. Another patent (101) has been issued to the same company for the uncatalyzed oxidation of *p*-alkylbenzoic acids at 370-550 °F. Still another (102) concerns the utilization of partially oxidized alkyl aromatic hydrocarbons, i.e. carbinols, ketones, and oxygen-containing compounds in general, by treatment with elemental sulphur in aqueous alkaline medium. The material is converted to acids.

It appears, therefore, that such a great deal of effort has been expended in industrial laboratories in the last few years on the preparation of terephthalic acid, particularly by oxidation, that it is doubtful whether this aim of our cymene work warrents much further investigation.

APPENDIX 1

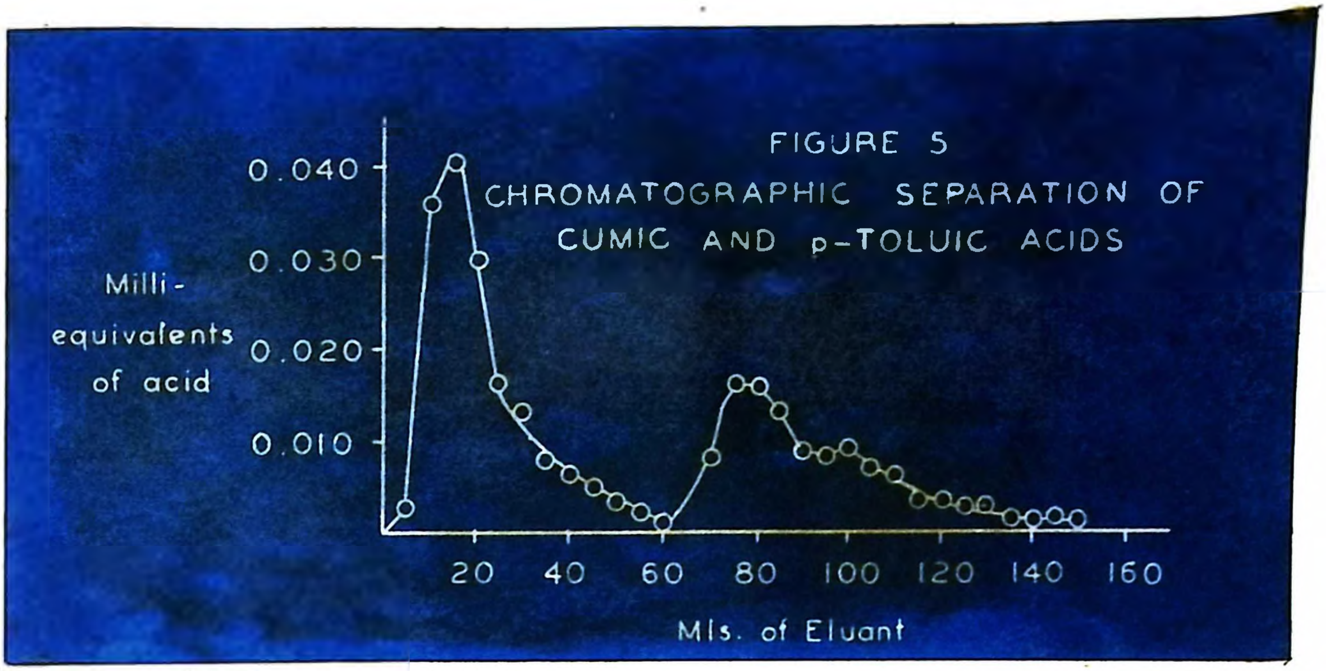
Chromatographic Separation of Cumic and p-Toluic Acids

A small column, containing 20 g. of silicic acid and proportionate amounts of indicator solution, methanol, and ammonium hydroxide (see Table III, p.92), was prepared in the manner described in the EXPERIMENTAL section. Petroleum ether was used as the eluent. p-Toluic acid (0.0169 g.) and cumic acid (0.0293 g.) were dissolved in a little petroleum ether, the solution placed on to the column and the chromatogram developed as previously described.

The two visible bands followed one another rather closely and rapidly down the column, cumic acid coming first. When the first band neared the bottom, the eluted liquid was collected in 5 ml. portions in 30 ml. Erlenmeyer flasks and the collection procedure was continued until both bands had been completely eluted. To each fraction was added one drop of 0.01 per cent phenol red indicator solution and one drop of 2 per cent Dreft solution. The emulsions were magnetically stirred and titrated with 0.02 N sodium hydroxide (88).

A plot of milliequivalents of acid per fraction vs. volume of eluent, Figure 5, shows that excellent separation was obtained. Recovery was nearly quantitative.

Since cumic acid was not obtained in a very pure condition from the main chromatograms of the "primary acid



products" of Runs 4 and 6, it was thought possible that p-toluic acid might be present in the cumic acid band, though undetected. Cumic and p-toluic acids are alike in that the non-acidic side chains are aliphatic and relatively non-polar in nature compared to the keto-, hydroxy-, and hydroperoxy-groups. Rechromatograms of cumic acid fractions in columns employing petroleum ether as eluent, however, gave no indication of the presence of toluic acid. This fact, combined with the very clean separations obtained in repeated analyses of synthetic mixtures of the two acids, clearly established that p-toluic acid is present in the acid product either not at all, or only in very small amounts.

APPENDIX 2

Hydroperoxide Analysis

An iodometric procedure suggested to us by Hercules Powder Co., Wilmington, Delaware (103), was used for the analysis of hydroperoxide in all samples. This method is based upon the oxidation of iodide to free iodine by the hydroperoxide.

$$ROOH + 2I^{-} + 2H \longrightarrow I_2 + ROH + H_2O$$

The liberated iodine is then determined by titration with standard thiosulphate solution.

In determining the amount of hydroperoxide present in the reaction product of an autoxidation, small samples (0.3-0.4 g.) were used, while for characterization of the solid p-(α-hydroperoxyisopropyl)benzoic acid, samples as small as 50 mg. were found quite satisfactory. In each case the sample was weighed into a 250 ml. standard taper Erlenmeyer flask, and 100 ml. of isopropanol was added together with 10 ml. of glacial acetic acid and 1 ml. of saturated potassium iodide solution. The flask was connected to a reflux condenser and the solution was heated gently on a low flame for three or four minutes. The condenser was washed down with 10 ml. of isopropanol and the sides of the flask rinsed with 25 ml. of distilled water. The liberated iodine was titrated with 0.05 N sodium thiosulphate solution to the disappearance of the yellow color.[a] Blank determinations carried out were of the order 0.1 ml.

Since hydroperoxide present in the oxidation mixture consisted of three possible compounds, $p\text{-}(CH_3)_2CHC_6H_4CH_2OOH$, $p\text{-}(CH_3)_2C(OOH)C_6H_4CH_3$, and $p\text{-}(CH_3)_2C(OOH)C_6H_4COOH$, the calculations were made for per cent of peroxidic oxygen, i.e., both oxygens of ROOH.

$$\text{Per Cent Peroxidic Oxygen} = \frac{\text{ml. thio. x N. thio. x 100 x 32}}{\text{2 x sample weight x 1000}}$$

Since only one of these compounds was considered present in the acid products, however, the calculations were made for the percentage of hydroperoxy-acid ($C_{10}H_{12}O_4$).

$$\text{Per Cent Hydroperoxy-Acid} = \frac{\text{ml. thio. x N. thio. x 100 x 196.2}}{\text{2 x sample weight x 1000}}$$

In the characterization of the hydroperoxy-acid the equivalent weight of the acid was calculated as follows:

$$\text{Equivalent Weight} = \frac{\text{2 x sample weight x 1000}}{\text{ml. thio. x N. thio.}}$$

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[a] Soluble starch failed as an indicator under these conditions, but isopropanol intensifies the color of free iodine to provide a sharp end point.

APPENDIX 3

Chromatographic Data and Results

The results of the individual chromatograms from which the yields of the four acid products were calculated, are presented in some detail in Tables VII and VIII for Runs 4 and 6, respectively. For each chromatogram the sample weights actually used are given, together with the weights of components recovered. In the lower right hand corner of each table are the total analysis figures obtained by calculation.

The recovery of cumic acid in Analysis C 31, Run 4, for example, was 47.70 per cent of the sample chromatographed. In the total "primary acid product" of 28.0 g., therefore, there was 47.70 per cent of 28.0 g., or 13.35 g. of cumic acid. The sample obtained, however, was impure and some of it was rechromatographed in Analysis C 36 resulting in a purer product in 96.5 per cent recovery. Most of the remainder was oils. The final yield for cumic acid in Run 4 was then 96.5 per cent of 13.35, or 12.9 g.

Table VII

CHROMATOGRAPHIC RESULTS - RUN 4

	Analysis C 31 (A)[a] Primary Acid Product (28.0 g.) Amount recovered (g.)	(%)	Analysis C 36 (B_3) Repeat Band 1, C 31 Amount recovered (g.)	(%)	Analysis C 42 (B_1) Repeat Band 2, C 31 & midband following Amount recovered (g.)	(%)
Sample	1.8887	-	0.1035	-	0.0508	-
Band 1 (RH)	0.9012	47.70	0.1000	96.5	-	-
Midband	0.0159	0.84	0.0026	2.5	-	-
Band 2 (RC=O)	0.0446	2.36	-	-	0.0442	87.0
Midband	0.0303	1.60	-	-	0.0037	7.3
Band 3 (ROOH)	0.2604	13.78	-	-	-	-
Band 4 (ROH)	0.6052	32.08	-	-	-	-
Total recovered	1.8576	98.36	0.1026	99.0	0.0479	94.3

	Analysis C 24 (B_1) Secondary Acid Product (1.3 g.)				Total Analysis (29.3 g.)	
Sample	0.0988	-				
Band 1	-	-			12.9	44.0
Midband	-	-			0.5	1.7
Band 2	0.0152	15.4			1.2	4.1
Midband	-	-			0.1	0.3
Band 3	-	-			3.9	13.3
Band 4	0.0719	72.8			9.9	33.8
Total recovered	0.0871	88.2			28.5	97.2

a. The letters in parentheses after the "Analysis" numbers refer to the different types of columns (see Table III, p.92).

Table VIII

CHROMATOGRAPHIC RESULTS - RUN 6

	Analysis C 32 (A)[a] Primary Acid Product (20.8 g.) Amount recovered (g.)	(%)	Analysis C 35 (B_1) Repeat Band 1, C 32 Amount recovered (g.)	(%)	Analysis C 37 (B_2) Repeat Band 1, C 35 Amount recovered (g.)	(%)
Sample	1.7979	-	0.1029	-	0.0927	-
Band 1 (RH)	1.2551	69.80	0.0927	90.1	0.0880	95.0
Midband	0.0229	1.27	0.0078	7.6	0.0050	5.4
Band 2 (RC=O)	0.1688	9.39	-	-	-	-
Midband	0.0159	0.89	-	-	-	-
Band 3 (RCOOH)	-	-	-	-	-	-
Band 4 (ROH)	0.3120	17.36	-	-	-	-
Total recovered	1.7747	98.71	0.1005	97.7	0.0930	100.4

	Analysis C 40 (B_1) Repeat Band 2, C 32		Analysis C 29 (B_1) Secondary Acid Product (1.8 g.)		Total Analysis (22.6 g.)	
Sample	0.0502	-	0.0961	-		
Band 1	-	-	-	-	12.4	54.9
Midband	0.0053	10.6	-	-	2.3	10.2
Band 2	0.0418	83.4	0.0126	13.1	1.8	8.0
Midband	0.0016	3.2	-	-	0.3	1.3
Band 3	-	-	-	-	-	-
Band 4	-	-	0.0753	78.5	5.0	22.1
Total recovered	0.0487	97.2	0.0879	91.6	21.8	96.5

a. The letters in parentheses after the "Analysis" numbers refer to the different types of columns (see Table III, p.92).

APPENDIX 4

Calculation of Converted Cymene from Oxygen Consumption Data

The weight of oxygen gas taken up in each oxidation was calculated from air flow rates and periodic analyses for oxygen in the exit gas. A considerable proportion of the oxygen can be accounted for in the identified products, namely, the four acids, water, and carbon dioxide. As to the remainder, the assumptions listed on p.105 were made, and the calculations were carried out as follows:

Run 4

Known oxygen:

Cumic acid	(12.9 x 32/164.2)	2.51 g.
Keto-acid	(1.2 x 48/164.2)	0.35 g.
Hydroperoxy-acid	(3.9 x 64/196.2)	1.27 g.
Hydroxy-acid	(9.9 x 48/180.2)	2.64 g.
Oils and losses (1.4 g.)	(Assumption a)	0.4 g.
Water		0.5 g.
Carbon dioxide		0.0 g.
Hydroperoxide in "Liquid Product"	(5.13% of 159.7 =8.2) (8.2 x 32/166.2) (Assumption b)	1.58 g.
Total		9.3 g.
Total oxygen uptake		18.5 g.
Oxygen in "Liquid Product" as ketone and carbinol	(Assumption c)	9.2 g.

Since the "liquid product" is assumed to contain 0.865 moles of p-methylacetophenone for every mole of dimethyl-p-tolylcarbinol (Assumption c), the 9.2 g. of oxygen will be distributed 9.2 x 0.865/1.865 = 4.27 g. in the ketone and 9.2 x 1/1.865 = 4.94 g. in the carbinol.

The content of the "liquid product" is now directly calculable:

Hydroperoxide	(5.13% of 159.7)	8.2 g.
Ketone	(4.27 x 134.2/16.0)	35.8 g.
Carbinol	(4.94 x 150.2/16.0)	46.4 g.
p-Cymene	(by difference)	69.3 g.
Total	(weighed)	159.7 g.

The figure for converted cymene is then the difference between hydrocarbon charged (167.8 g.) and the above figure for cymene in the "liquid product" (69.3 g.), namely 98.5 g. This is in good agreement with the figure for converted cymene obtained as the difference between hydrocarbon charged and hydrocarbon recovered from the "liquid product" by fractional distillation: 167.8 - 75.8 = 92.0 g.

The composition of the "liquid product" for Run 6 was similarly calculated from oxygen consumption data with the following results:

Ketone		47.0 g.
Carbinol		61.0 g.
p-Cymene	(by difference)	59.6 g.
Total	(190.2 - 22.6)	167.6 g.

Converted cymene was then 167.8 - 59.6 = 108.2 g.

The yields of individual acid products for both runs were calculated in the usual manner.

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