# HYDROCARBON AUTOXIDATION

CHARLES E. FRANK

*Graduate Department of Applied Science, University of Cincinnati, Cincinnati, Ohio*

*Received July 29, 1949*

CONTENTS

## I. INTRODUCTION

The difficult problem of controlled hydrocarbon autoxidation[1] is receiving increasing attention in both academic and industrial research. Earlier oxidations of industrial importance were limited largely to the production of highly stable products, such as phthalic anhydride, where no considerable degree of selectivity was required. More recently a limited degree of control has been realized, as evidenced by the present commercial production of formaldehyde and acetaldehyde from natural gas and of cyclohexanone from cyclohexane. However, enormous potentialities of selective hydrocarbon oxidation as a general, low-cost, synthetic tool remain undeveloped. The present discussion attempts to summarize the status of liquid-phase hydrocarbon autoxidation and to point out some of the problems to be solved in achieving a better understanding of the process.

Hydrocarbon autoxidation in the liquid phase consists of two distinct reaction sequences (31). The first of these is a relatively simple, free-radical chain reaction resulting in the formation of a hydroperoxide. Some hydroperoxides are so stable that the reaction can be stopped at this point and the peroxide isolated in satisfactory yield; examples of these are the hydroperoxides from cyclohexene, tetralin, and decalin. More commonly, however, the hydroperoxide is unstable and passes quickly into the second phase of the reaction, hydroperoxide decomposition. This fact complicates enormously the study of autoxidative processes, since fragments formed by the decomposition of the peroxide may serve as

---

[1] The term "autoxidation" is used here as defined by Waters (36), that is, in referring to "oxidations which can be brought about by oxygen gas at normal temperatures without the intervention of a visible flame or of an electric spark."

initiators for further oxidative attack on the hydrocarbon, or, on the other hand, may react with radicals formed during the first phase to reduce the efficiency of the oxidative attack. As Waters has pointed out (35), the mechanism of hydroperoxide decomposition is strongly dependent upon the environment; thus, there is good evidence that decomposition can proceed by both free-radical and ionic mechanisms. It becomes apparent that the environment of an autoxidation has a dual effect of utmost importance in promoting and directing the reaction; it likewise is obvious that a better understanding of the effect of environment on the mechanism of hydroperoxide decomposition will advance markedly our control over autoxidation processes.

## II. THE FIRST PHASE OF THE REACTION

A large amount of evidence has accumulated demonstrating clearly that the attack of elementary oxygen on a hydrocarbon is a free-radical chain reaction (2, 3, 35, 36). Activation may be accomplished by light, heat, metallic ions, or by a variety of molecules which decompose to give free radicals under reaction conditions; the wide range of possible activating agents is illustrated by the recent finding that hydrogen atoms can initiate autoxidation (5). Conversely, autoxidation is inhibited by small amounts of "antioxidants," such as phenols and amines which give resonance-stabilized radicals. As in other chain reactions, the general sequence of oxidative attack comprises initiation, propagation, and termination:

*Initiation:*[2]

$$RH \xrightarrow{\text{activation}} R\cdot + (H\cdot) \tag{1}$$

*Propagation:*

$$R\cdot + O_2 \rightarrow RO_2\cdot \tag{2}$$

$$RO_2\cdot + RH \rightarrow RO_2H + R\cdot \tag{3}$$

*Termination:*

$$R\cdot + R\cdot \rightarrow RH + R(\text{—}H) \tag{4}$$

$$RO_2\cdot + \cdot OH \rightarrow ROH + O_2 \tag{5}$$

$$R\cdot + R\cdot \rightarrow R\text{—}R \tag{6}$$

etc.

### *A. Initiation; the induction period*

The role of peroxides and other compounds capable of generating free radicals as oxidation initiators is apparent from a consideration of equation 1. Similarly, light or heat of sufficient energy to "activate" an appreciable number of hydrocarbon molecules will initiate the reaction. For example, the ability of light to initiate hydrocarbon oxidation is illustrated by a recent patent (42) reporting the ultraviolet-light-catalyzed oxidation of olefins to hydroperoxides, ketones, aldehydes, and acids at temperatures of −50° to 150°C.

---

[2] Equation 1 is the general expression for reaction initiation. Activation at moderate temperatures resulting from the impact of a radical or molecule of high energy content yields, for example, $R\cdot + R'H$ or $R\cdot + \cdot OOH$ where the initiator is $R'\cdot$ or $O_2$, respectively.

Frequently, the initiation of a low-temperature hydrocarbon autoxidation is preceded by an induction period; such an induction period may result for very different reasons. If the hydrocarbon is very pure, considerable time may be required to build up a sufficient peroxide concentration to sustain the chain reaction. Hock (20) observed that cyclohexene which had stood for some time (peroxide present) was oxidized much more rapidly than freshly distilled material. Similarly, Robertson and Waters (28) noted that pure tetralin at 76°C. had an induction period of some hours, but that the addition of a few per cent of tetralyl hydroperoxide eliminated the induction period completely. On the other hand, the hydrocarbon may contain impurities which prevent the initiation of hydrocarbon autoxidation. Similar to inhibitors in addition polymerization, these "antioxidants" interrupt the reaction chain through the formation of resonance-stabilized radicals; Waters (35) has pointed out that inhibitors should be regarded as destroyers of the peroxide radicals ROO·, not of the hydroperoxide molecules ROOH. It is of interest that phenols and alcohols, which greatly extend the induction period of an autoxidation, generally have little effect on a reaction which is well under way (12, 28). As Robertson and Waters (29) have observed, only the most easily oxidizable phenols such as $\alpha$-naphthol are effective inhibitors after an appreciable amount of hydroperoxide has been formed. An excellent example of the effect of certain impurities on autoxidation is found in the prolonged protection afforded gasoline, rubber, and other products by the incorporation of traces of antioxidants.

The best known catalysts for liquid-phase autoxidation are the soluble derivatives of the transition metals,—for example, naphthenates and stearates of cobalt, manganese, copper, nickel, and iron. These catalysts have a dual role in hydrocarbon oxidation, that of initiation and that of hydroperoxide decomposition. The second of these will be considered later; however, it should be recognized at the outset that, by catalyzing decomposition of the hydroperoxide, the metallic catalyst promotes the generation of radicals which will initiate further attack on the hydrocarbon. This fact is of primary importance after the reaction has reached a steady state, but it does not explain how the catalyst reduces or eliminates the induction period in the oxidation of a pure hydrocarbon. It is apparent that the metallic ion is capable of extracting a hydrogen just as in other means of "activation." Waters (37) notes that chromic acid and permanganate are immediate catalysts for tetralin autoxidation and therefore must form tetralyl radicals by abstraction of a hydrogen atom. George and Robertson (17), in a study of oxidation catalyzed by heavy metals, conclude that the catalyst initiates the reaction chain by activating the oxygen. It may be that the exact activation mechanism will differ for different reactions, but the crux of the matter appears to lie in the ease with which the metal undergoes a single electron transfer and thereby produces free radicals, although itself not a free radical.

Some additional information on the action of metal catalysts is contained in a report of the I. G. Farbenindustrie on the oxidation of cyclohexane (4). In the presence of cobalt naphthenate catalyst, the oxidation of cyclohexane occurs readily at 120–130°C.; the concentration of peroxide remains at a very low level throughout the reaction. In the absence of a metal catalyst, the oxidation proceeds at a comparable rate at 140–150°C. after a considerable induction period; during the uncatalyzed reaction the concentration of peroxide builds up to about 3.5 per cent. Substantially the same products are obtained from the two reactions.

### *B. Propagation*

Equations 2 and 3 represent the propagation steps of the reaction. The fact that even the inactive triphenylmethyl radical combines instantly with atmospheric oxygen demonstrates the ease of reaction 2. Cleavage of the R—H bond by $RO_2\cdot$ in equation 3 does not occur nearly so readily (24), and it is here, as well as in equation 1, that the less easily oxidizable hydrocarbons, such as cyclohexane, contrast with those hydrocarbons (like tetralin) containing activated hydrogen atoms. In an autoxidation which is proceeding smoothly at a steady state, the oxidizing hydrocarbon is seen to be regenerating its own initiator just as in addition polymerization.

### *C. Termination*

As in addition polymerization, the termination step of an autoxidation may be any of several possibilities, for example, equations 4, 5, and 6. In a study of tetralin oxidation, Robertson and Waters (31) concluded that the major chain-terminating step in the early stages of oxidation is that of disproportionation (equation 4), while the removal of $RO_2\cdot$ (for example, by reaction with $\cdot OH$ as in equation 5) is the major factor later in the reaction. The importance of reactions such as equation 6 (15) in chain termination varies with the structure of the hydrocarbon and the reaction conditions. In general, a resonance-stabilized radical would be expected to yield more dimer (R—R) than a more active radical. Small amounts of 2,3-diphenylbutane are formed in the autoxidation of ethylbenzene (12), while the low-temperature autoxidation of various substituted 4-nitrotoluenes is a useful preparation of the corresponding dibenzyl and stilbene derivatives (32). On the other hand, Robertson and Waters failed to isolate any ditetralyl from the oxidation of tetralin (31).

The effect of inhibitors (antioxidants) on hydrocarbon oxidation, already discussed from the standpoint of initiation, also is a factor in the reaction termination. This effect will depend upon whether a steady supply of free radicals (chain initiators) is being generated in sufficient number to overcome the chain-breaking action of the inhibitor. The view that the action of inhibitors is a relative rather than an absolute effect is substantiated by the experimental evidence. For example, as noted earlier, compounds which completely prevent initiation of an oxidation may have little effect on a reaction which has reached a steady state (12, 28). Just as in polymerization, the phenols and amines act as chain breakers by the formation of radicals too inactive to carry on the propagation chain. It has been proposed by Robertson and Waters (28) that the inhibiting action observed for alcohols and water during metal-catalyzed autoxidation may be the result of the following equilibrium (equation 7), which removes $ROO^-$ from the radical-forming process (equation 8):

$$ROO^- + R'OH \rightarrow ROOH + RO^- \qquad (7)$$
$$ROO^- + M^{++} \rightarrow ROO\cdot + M^+ \qquad (8)$$

Emerson (12) suggests that the inhibition by water is due to a deactivation of the metal catalyst brought about by combination with the polar water molecules. In the absence of metal catalyst, Robertson and Waters (28) postulate that the inhibiting action of alcohols may be explained by the following equilibrium:

$$R'OH + \cdot OH \rightarrow RO\cdot + H_2O \qquad (9)$$

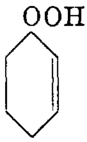
This explanation assumes that the chain propagation by $\cdot OH$ is more rapid than that by $\cdot OR$, although in a subsequent paper (31) the same authors estimate that the $\cdot OR$ radical is sufficiently active to attack most C—H bonds. The role of the various types of inhibitors in oxidation reactions still has not been explained adequately; since all hydrocarbon oxidations give rise to one or more types of possible inhibitors (water, alcohols, phenols), the effect of these products on the subsequent oxidation merits considerable attention.

### *D. Point of oxidative attack*

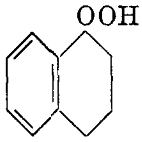
In considering the most likely point of oxidative attack, it should be noted that a marked difference is observed in gas-phase *versus* liquid-phase reaction, and in high-temperature *versus* low-temperature reaction. Thus, in the gas phase at 200–265°C. the straight-chain paraffins have been found (11) to undergo oxidation more readily than the corresponding branched-chain hydrocarbons. However, at more moderate temperatures and in the liquid phase a slower and more selective reaction occurs; thus, Walsh (33, 34) and others have found that the tertiary C—H bond is attacked in preference to the secondary C—H bond, and the secondary in preference to the primary. There appears to be no doubt that different oxidative mechanisms obtain under different reaction conditions (11, 34, 38). This is reasonable to expect when one considers that the radical which sustains the main reaction chain under one set of conditions may be replaced almost entirely under other conditions by a radical having very different reactivity. In addition, the reactivity of a given radical will vary markedly with reaction conditions, for example, as observed by Milas in a study of the hydroxyl radical (25).

In the liquid phase at temperatures up to about 150°C. the generalization that the tertiary C—H is attacked most easily and the primary C—H with most difficulty appears to hold. This is in line with the general prediction that the most stable free radical will be the one formed. As demonstrated by the work of Farmer (13, 14), Hock (20), and Criegee (8), the still more facile attack on an olefin is not at the double bond, but at the adjacent activated methylene group.

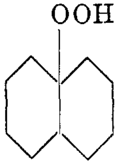
Isolation of the following hydroperoxides from low-temperature autoxidation illustrates these generalizations:



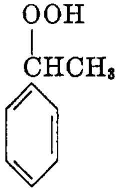
(8, 20)



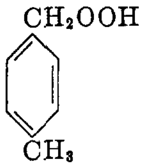
(23, 28)



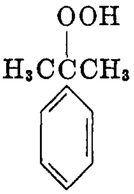
(9)



(21)

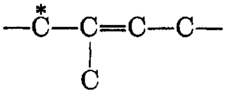


(21)

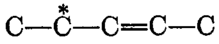


(22)

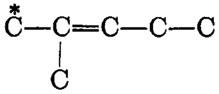
From his work on the oxidation of various olefinic substances, Farmer (13) indicates* the most vulnerable points of attack in the following structures:



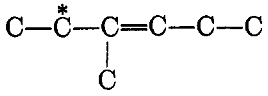
$$-\overset{*}{C}-\underset{\substack{|\\ C}}{C}=C-C-$$



$$C-\overset{*}{C}-C=C-C$$



$$\overset{*}{C}-\underset{\substack{|\\ C}}{C}=C-C-C$$



$$C-\overset{*}{C}-\underset{\substack{|\\ C}}{C}=C-C-C$$

A further indication of the relative ease of oxidative attack on various structures is afforded by the work of George and Robertson (16) on the rate of oxidation (roughly a measure of the strength of the weakest C—H bond) for a number of representative hydrocarbons. As listed in table 1, the rate measurement was the amount of oxygen absorbed by the hydrocarbon at 110°C., using 0.5 per cent copper stearate catalyst.

### III. THE SECOND PHASE OF THE REACTION

Turning to the second phase of hydrocarbon autoxidation, that of hydroperoxide decomposition, the following possible mechanisms merit consideration:

*Free-radical:*

$$ROOH \rightarrow RO\cdot + \cdot OH \tag{10}$$

*Acid-catalyzed:*

$$ROOH \rightarrow RO^{+} + OH^{-} \tag{11}$$

*Base-catalyzed:*

$$ROOH \rightarrow ROO^- + H^+ \qquad (12)$$

*Metal-catalyzed:*

$$ROOH \xrightarrow{M^+} RO^- + \cdot OH\ (+ M^{++}) \qquad (13)$$

### *A. Free-radical decomposition*

Hydroperoxides break down by thermal scission to give free radicals, as shown in equation 10 (2, 3, 35, 36). In general, their thermal stability is in line with their ease of formation. Thus, tertiary hydroperoxides are the most stable, secondary next, and primary least stable. Conjugation with a double bond also makes for stability, as is apparent from a comparison of cyclohexenyl hydroperoxide (readily isolated) with cyclohexyl hydroperoxide (reported only in solution (4)).

TABLE 1

*Rates of hydrocarbon autoxidation (16)*

| HYDROCARBON | OXYGEN PER MILLILITER OF HYDROCARBON PER HOUR |
|---|---|
| | *ml.* |
| Tetralin | 125 |
| 1,3,5-Trimethylcyclohexane | 11.2 |
| Ethylbenzene | 7.5 |
| Isopropylbenzene | 6.0 |
| Decalin | 4.3 |
| Paraffins ($C_{15}$–$C_{25}$) | 0.25 |

As pointed out by George and Walsh (18), thermal decomposition of a tertiary hydroperoxide can occur by initial scission of the O—O bond, and subsequent scission of the weakest C—C bond on the α-carbon atom. The following are typical examples of this decomposition:

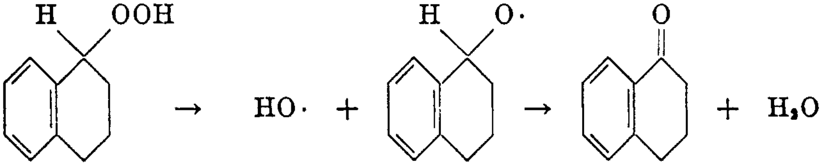
$$(C_6H_5)_3COOH \rightarrow \cdot OH + (C_6H_5)_3CO\cdot \rightarrow (C_6H_5)_2CO + C_6H_5\cdot \qquad (14)$$

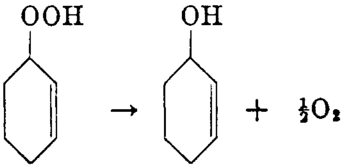
$$(CH_3)_3COOH \rightarrow \cdot OH + (CH_3)_3CO\cdot \rightarrow (CH_3)_2CO + (CH_3)\cdot \qquad (15)$$

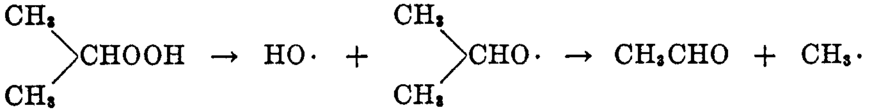
$$(CH_3)_2(C_6H_5)COOH \rightarrow \cdot OH + (CH_3)_2(C_6H_5)CO\cdot \rightarrow (CH_3)_2CO + C_6H_5\cdot \qquad (16)$$

Equation 16 recently has been reported as the basis of a new process of the Hercules Powder Company for the production of phenol and acetone (1); the cumene hydroperoxide is said to be catalytically decomposed at relatively low temperatures, the phenol resulting from a recombination of the phenyl and hydroxyl radicals. Thermal decomposition of tertiary hydroperoxides frequently follows a different course, however, and is influenced markedly by temperature. Milas and Surgenor (26) have found, for example, that *tert*-butyl hydroperoxide decomposes smoothly at 95–100°C. to give an 86 per cent yield of *tert*-butyl alcohol and a 91 per cent yield of oxygen; at 250°C. the peroxide decomposes explosively to yield 39 per cent acetone, 11 per cent *tert*-butyl alcohol, 7 per cent methanol, 10 per cent water, formaldehyde, and a little tar.

The thermal decomposition of a secondary hydroperoxide also may proceed by several courses (33, 34); depending upon conditions, the major product may be the ketone, the alcohol, or a degradation product resulting from C—C cleavage as with the tertiary hydroperoxides. These are illustrated by the following:


(17)


(18)


(19)

$$(CH_3)_2CHOOH \rightarrow HO\cdot + (CH_3)_2CHO\cdot \rightarrow CH_3CHO + CH_3\cdot \quad (19)$$

Walsh (33) states that a surface facilitates the less drastic decomposition, since after scission of the O—O, the ·OH and·OR radicals remain close for sufficient time to permit interaction yielding a ketone and water (equation 17); in the gas phase the RO· and ·OH radicals fly apart and the RO· subsequently decomposes (equation 19).

There is little direct experimental data on the decomposition of primary hydroperoxides because of the difficulty of isolating and working with these unstable products. The following decomposition mechanisms appear most probable (33, 34):

$$RCH_2OOH \rightarrow HO\cdot + RCH_2O\cdot \rightarrow RCHO + H_2O \quad (20)$$

$$RCH_2OOH \rightarrow RCH_2O\cdot \rightarrow R\cdot + HCHO \quad (21)$$

Equation 21, like equation 19, represents a reaction more likely at high temperatures in the gas phase than at the relatively low temperatures under consideration here. In all these considerations of hydroperoxide decomposition, it should be kept in mind that decomposition of the peroxy radical also may occur before the radical has seized a hydrogen atom (34):

$$RCH_2OO\cdot \rightarrow RCHO + \cdot OH \quad (22)$$

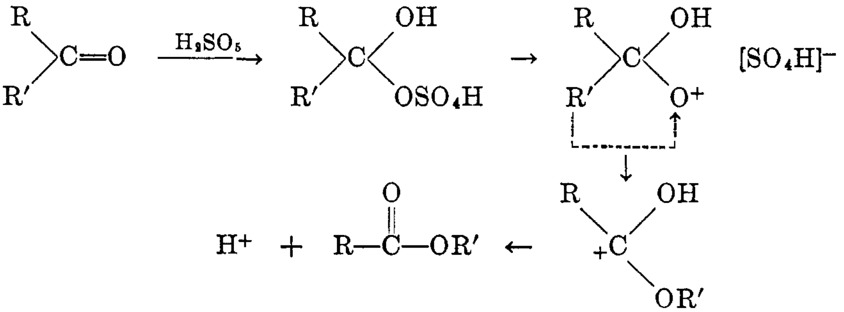
The alternative decomposition reaction (equation 23) also should be considered, particularly in view of the relative strengths of the C—C and C—H bonds:

$$RCH_2OO\cdot \rightarrow HCHO + RO\cdot \qquad (23)$$

### *B. Acid-catalyzed decomposition*

In the large volume of patent literature relating to hydrocarbon autoxidation, there are many indications that the reaction medium has a marked influence on the products obtained. For example, the cobalt-catalyzed oxidation of cyclohexane in acetic acid solution yields mainly adipic acid (48), whereas under similar conditions but in the absence of acetic acid the product is largely cyclohexanone and cyclohexanol (49). References to the incorporation of basic compounds in the reaction mixture to stop the oxidation at the desired stage also indicate that the reaction medium (acidic, neutral, or basic) has a definite effect on the course of hydrocarbon autoxidation (40, 41, 43, 45). Paquot (27) reports that the oxidation of cyclohexene in the absence of solvents gives principally oxidation at the α-methylene group; in acetic acid solution, oxidation is accompanied by rearrangement to the cyclopentene nucleus.

In general, hydrocarbon autoxidation in acidic solution tends to proceed beyond the ketone–alcohol stage to yield carboxylic acids as the major products. It is apparent at the outset that, since any such reaction proceeds stepwise, we must consider the effect of the acid on the intermediate compounds. From their study of the oxidation of tetralin, Robertson and Waters (29) suggest that the reaction of Caro's acid with cyclohexanone presents the clue to the mechanism involved. This reaction (6) results in the formation of caprolactone; it has since been extended to other ketones, and to other peroxy acids including peroxyacetic and peroxybenzoic. The following mechanism is proposed by Robertson and Waters:

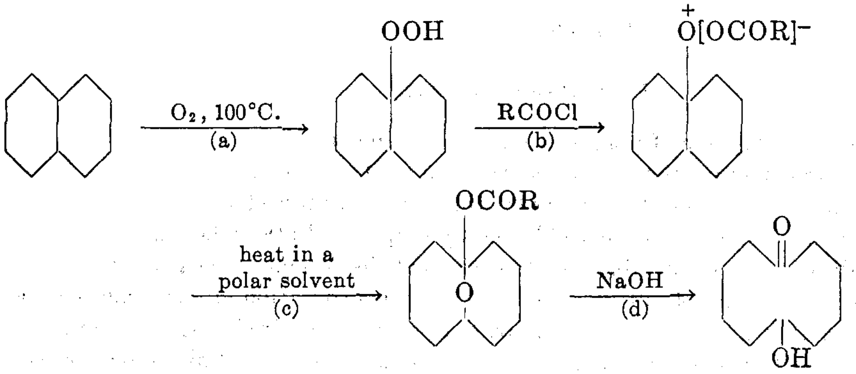


(24)

The driving force in the rearrangement is the electron deficiency of the oxygen atom; this explanation is in complete accord with Whitmore's well-known theory of intramolecular rearrangements.

Probably the most striking demonstration of the ionic mechanism of peroxide decomposition is found in the work of Criegee on the oxidation of decalin (10).

Criegee carried out the following series of reactions to attain a new route to the cyclodecane series:



(25)

The rearrangement in (c) is exactly analogous to the rearrangement involved in the transformation of cyclohexanone to caprolactone.

The above reactions leave little doubt as to the ionic nature of hydroperoxide decomposition in acidic solution. Heterolytic cleavage of the O—O bond leads to an *oxonium ion* which is stabilized by rearrangement of a hydrocarbon radical with accompanying scission of the C—C bond. The ester resulting from the subsequent loss of a proton may be isolated, or it may be hydrolyzed in the reaction mixture. Such a mechanism readily accounts for the oxidation of cyclohexane (through ω-hydroxycaproic acid) to adipic acid in acid solution (48), whereas neutral solution leads largely to cyclohexanone and cyclohexanol (49). Since the formation of a small amount of acid in an oxidizing mixture will serve to promote the formation of progressively larger amounts as the reaction progresses, the mechanism also accounts for the use of basic materials (acid acceptors) to obtain better yields of hydroperoxides, ketones, and alcohols in hydrocarbon autoxidation (40, 41, 43, 45).

### *C. Base-catalyzed decomposition*

While all of the mechanisms proposed above for the free-radical, acid-catalyzed, and metal-catalyzed decompositions of hydroperoxides have been suggested previously, there appears to have been little or no investigation of the role of alkalies in hydrocarbon autoxidation. Salt formation has been used as a means of isolating the pure hydroperoxide; this procedure can be employed, however, only in cold solution with the most stable of these compounds.

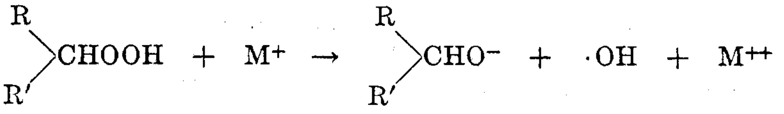
In warm alkali, hydroperoxides decompose rapidly with the formation of the alcohol (13, 20). For example, when cyclohexenyl hydroperoxide is shaken with dilute alkali, cyclohexenol is formed in 80 per cent yield (13); the remaining 20 per cent consists of hydroxy acids and dibasic acids. Farmer and Sundralingam (13) suggest that the oxidative action promoted by alkali is due to the hydrogen peroxide formed by hydrolysis of the hydroperoxide. Since hydroperoxides are weak acids, it is probably more exact to consider the formation of a *peroxide anion* (equation 12) as the first step. Decomposition of this anion in aqueous solution would yield the alcohol and the $^{-}$OOH anion (or atomic oxygen).

The potency of these fragments in initiating further oxidative attack appears to be strongly dependent upon temperature; thus, while cyclohexenyl hydroperoxide has given 80 per cent yields of the alcohol when decomposed by alkali at room temperature, these yields apparently fall off rapidly as the temperature is raised. In addition, the ability of alkalies to promote strongly degradative autoxidations at high temperatures is well known. The data are too scanty to permit more than speculation as to the role of alkalies in the reaction, but there can be little doubt that alkalies, like acids, may exert a selective effect on the course of hydroperoxide decomposition.

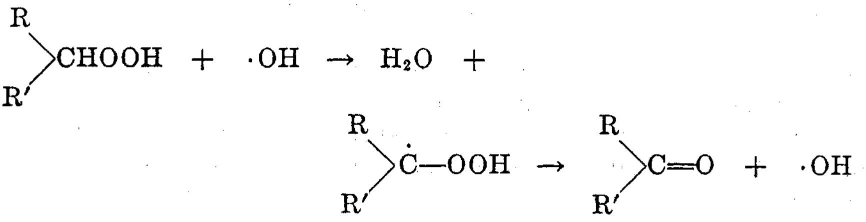
Certain other references to the use of alkalies in autoxidations should be noted. As already mentioned, a number of patents (40, 41, 43, 45) report basic compounds as regulators or "softeners" for the reaction; in these instances the basic compounds probably act as acid acceptors rather than alkaline catalysts. Another reaction involving the use of alkali is found in the coupling of substituted 4-nitrotoluenes by autoxidation (32); here the most probable function of the alkali is to labilize the C—H bond of the methyl group and to enhance the stability of the nitrobenzyl radical.

### *D. Metal-catalyzed decomposition*

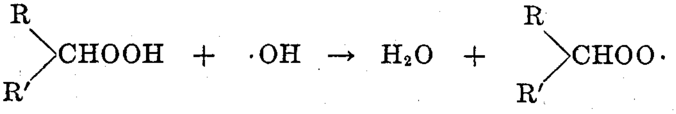
The ability of metallic ions to initiate hydrocarbon autoxidation has been discussed in an earlier section. In an oxidizing hydrocarbon solution, however, these catalysts also exercise a second role,—that of promoting peroxide decomposition. This dual function of metallic catalysts accounts for their remarkable potency, since unlike "initial catalysts" (free-radical initiators), which may be exhausted before the reaction is well established, these "secondary catalysts" (metallic ions) increase in activity until a steady state has been attained (28). It is proposed by Robertson and Waters (28) that this catalytic activity is the result of the following mechanism, based on the work of Haber and Weiss (19) on the ferrous ion-catalyzed decomposition of hydrogen peroxide:



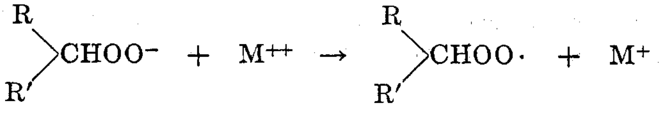
$$\mathrm{RR'CHOOH} + \mathrm{M^+} \rightarrow \mathrm{RR'CHO^-} + \cdot\mathrm{OH} + \mathrm{M^{++}} \tag{26}$$



$$\mathrm{RR'CHOOH} + \cdot\mathrm{OH} \rightarrow \mathrm{H_2O} + \mathrm{RR'\dot{C}{-}OOH} \rightarrow \mathrm{RR'C{=}O} + \cdot\mathrm{OH} \tag{27}$$



$$\mathrm{RR'CHOOH} + \cdot\mathrm{OH} \rightarrow \mathrm{H_2O} + \mathrm{RR'CHOO\cdot} \tag{28}$$



$$\mathrm{RR'CHOO^-} + \mathrm{M^{++}} \rightarrow \mathrm{RR'CHOO\cdot} + \mathrm{M^+} \tag{29}$$

Equation 26 represents scission of the O—O bond, forming an ion and a radical and oxidizing the metallic cation. Equations 27 and 28 represent two alternative attacks of the ·OH radical on the hydroperoxide, both reactions being chain-sustaining; reaction 27 appears the more likely of these. Equation 29 shows the regeneration of the reduced metallic cation, and explains why only a small amount of such a catalyst is required.

Experimental evidence regarding the types of products formed by metal-catalyzed peroxide decomposition is inconclusive. Robertson and Waters (30) report, for example, that cobalt naphthenate catalyzes the oxidation of tetralin but has no effect on the ketone–alcohol ratio obtained. Cook (7) states that iron phthalocyanine catalyzes the decomposition of tetralyl hydroperoxide to give largely the ketone. George, Rideal, and Robertson (15) found that iron phthalocyanine and copper stearate both catalyze peroxide decomposition largely to the ketone. It seems most probable that a careful study of hydroperoxide decomposition by various metallic catalysts at low temperatures will show that the various ions do promote selective hydroperoxide decomposition. Such an investigation should prove extremely fruitful in uncovering ways of attaining better control over oxidative processes.

## IV. CHAIN-TRANSFER PHENOMENA

During the course of this discussion we have noted many analogies between the two free-radical chain reactions, autoxidation and addition polymerization: initiation by free radicals, inhibition by "antioxidants," and a logical division into initiation, propagation, and termination phases. In conclusion, I should like to point out another analogy arising from the fundamental mechanism of free-radical chain reactions, the phenomenon of chain transfer. In autoxidation, chain transfer appears to manifest itself in two ways (exclusive of inhibition, which is a special case of chain transfer with the formation of an inactive radical): (*1*) a promoting effect in which the chain-transfer agent generates a radical more capable of sustaining attack on the RH than is the radical ROO·; (*2*) a moderating effect in which the chain-transfer agent deactivates the "excess" radicals (chain branching through the secondary decomposition of ROOH often leads to autocatalytic, uncontrollable reaction) and permits more selective control over the reaction.

There are a large number of references which indicate the existence of chain transfer in autoxidation reactions. An example of the promoting effect is found in the patents of Rust, Vaughan, and others assigned to the Shell Development Company (51–54). It is claimed that in liquid-phase or vapor-phase autoxidations, the presence of hydrogen bromide promotes oxidation at a much lower temperature than otherwise possible; presumably at these lower temperatures the bromine atom sustains the reaction chain much more effectively than does the radical ROO·. Examples of the moderating effect also are found in the patent literature (39, 44, 47, 50); a large number of compounds which would be expected to act as chain-transfer agents, including halogens, hydrogen halides, carbon tetrachloride, ethers, alcohols, etc., are claimed as "moderators," "selective repressants," and "protective agents" for various autoxidations. While satisfactory data to substantiate specific claims frequently are lacking, the large number of these claims does suggest the existence of this effect.

The fundamental concept of chain transfer leads to one additional prediction: namely, that the presence of one hydrocarbon may influence to a large degree the oxidation of another. George and Robertson (16) have pointed out that the oxygen uptake of autoxidation can be expressed as the chain initiation rate times the chain length, in which the chain length is the ratio: propagation rate/termination rate. If the chain initiation rate of hydrocarbon A is relatively low, it will act simply as a diluent when present in an oxidizing solution of hydrocarbon B. If, however, the chain length of A autoxidation is low, then A will act as a retarder when present in an oxidizing solution of hydrocarbon B. These effects were demonstrated by oxidizing mixtures of equal parts of ethylbenzene and a series of representative hydrocarbons at 110°C. in the presence of copper stearate catalyst. Table 2 summarizes a portion of this work. It is apparent that *tert*-butylbenzene at 110°C. has no effect on the oxidation of ethylbenzene, in agreement with its relative resistance to oxidative attack. Naphthalene and anthracene are effective inhibitors under these conditions, presumably through the formation of resonance-stabilized radicals. The slight inhibiting effects of ethylcyclohexane and *n*-octane are due probably to low rates of propagation, since either of these hydrocarbons should yield radicals more active than those resulting from ethylbenzene.

TABLE 2

*Autoxidation rates of hydrocarbon mixtures (16)*

| HYDROCARBON (MIXED WITH AN EQUAL AMOUNT OF ETHYLBENZENE) | OXYGEN PER MILLILITER OF HYDROCARBON PER HOUR | |
|---|---|---|
| | Rate observed | Rate calculated (assuming second hydrocarbon a diluent) |
| | *ml.* | *ml.* |
| Anthracene | 0 | 3.8 |
| Naphthalene | 0.1 | 3.8 |
| *tert*-Butylbenzene | 3.8 | 3.8 |
| Ethylcyclohexane | 4.0 | 4.5 |
| *n*-Octane | 3.3 | 3.9 |

In addition to the two situations outlined above there remains a third possibility: if the chain length for the autoxidation of hydrocarbon A is relatively high, then under conditions which satisfactorily initiate its reaction, the presence of A should increase the autoxidation rate of hydrocarbon B. A few examples of this phenomenon have been reported from studies of vapor-phase oxidations. Hinshelwood (11) found that 5–10 per cent of *n*-hexane markedly accelerates the oxidation of 3-methylpentane at 251°C. In the patent literature (46) it is claimed that the presence of cycloparaffins, paraffins, or olefins in small amounts improves the conversion to phenol in the high-temperature oxidation of benzene.

## V. REFERENCES

(1) Chem. Ind. **64,** March Newsletter (1949).
(2) Faraday Society: A General Discussion on Oxidation, Trans. Faraday Soc. **42,** 99–398 (1946).
(3) Faraday Society: A General Discussion on The Labile Molecule (1947).
(4) "Oxidation of Cyclohexane" (I. G. Farbenindustrie): T.O.M. Reel 22, Bar 3045, Item 68, Frames 680000835–845; Translation PC-7, Charles A. Meyer and Company, New York 17, New York.

(5) BADIN: J. Am. Chem. Soc. **70,** 3965 (1948).
(6) BAEYER AND VILLIGER: Ber. **32,** 3625 (1899).
(7) COOK: J. Chem. Soc. **1938,** 1774.
(8) CRIEGEE: Ber. **72,** 1799 (1939).
(9) CRIEGEE: Ber. **77,** 22 (1944).
(10) CRIEGEE: Ber. **77,** 722 (1944).
(11) CULLIS AND HINSHELWOOD: Reference 3, p. 117.
(12) EMERSON *et al.*: J. Am. Chem. Soc. **70,** 3764 (1948).
(13) FARMER *et al.*: J. Chem. Soc. **1942,** 121.
(14) FARMER *et al.*: Trans. Faraday Soc. **38,** 340, 348 (1942).
(15) GEORGE, RIDEAL, AND ROBERTSON: Proc. Roy. Soc. (London) **185,** 288 (1946).
(16) GEORGE AND ROBERTSON: J. Inst. Petroleum **32,** 400 (1946).
(17) GEORGE AND ROBERTSON: Reference 2, p. 217.
(18) GEORGE AND WALSH: Trans. Faraday Soc. **42,** 94 (1946).
(19) HABER AND WEISS: Proc. Roy. Soc. (London) **A147,** 333 (1934).
(20) HOCK AND GANICKE: Ber. **71,** 1430 (1938).
(21) HOCK AND LANG: Ber. **76,** 169 (1943).
(22) HOCK AND LANG: Ber. **77,** 257 (1944).
(23) HOCK AND SUSEMIHL: Ber. **66,** 61 (1933).
(24) MELVILLE: Reference 3, p. 2.
(25) MILAS, STAHL, AND DAYTON: J. Am. Chem. Soc. **71,** 1448 (1949).
(26) MILAS AND SURGENOR: J. Am. Chem. Soc. **68,** 205 (1946).
(27) PAQUOT: Bull. soc. chim. [5] **8,** 695 (1941).
(28) ROBERTSON AND WATERS: Reference 2, p. 201.
(29) ROBERTSON AND WATERS: J. Chem. Soc. **1948,** 1574.
(30) ROBERTSON AND WATERS: J. Chem. Soc. **1948,** 1578.
(31) ROBERTSON AND WATERS: J. Chem. Soc. **1948,** 1585.
(32) TREVES: J. Am. Chem. Soc. **70,** 875 (1948).
(33) WALSH: Reference 2, p. 269.
(34) WALSH: Trans. Faraday Soc. **43,** 297 (1947).
(35) WATERS: "Mechanisms of Oxidation," in Ann. Repts. on Progress Chem. (Chem. Soc. London) **42,** 130–57 (1945).
(36) WATERS: *The Chemistry of Free Radicals*, 2nd edition, pp. 226–58. Oxford University Press, London (1948).
(37) WATERS: Reference 36, p. 258.
(38) WATERS: Reference 36, pp. 244–5; reference 35, pp. 132, 134.

### *Patents*

(39) BERL: U. S. patent 2,270,779 (January 20, 1944).
(40) EMERSON AND HEYD: U. S. patent 2,447,400 (August 17, 1948).
(41) FARKAS AND STRIBLEY: U. S. patent 2,430,864–5 (November 18, 1947).
(42) GRAY, STEINER, AND PETROCARBON LTD.: British patent 614,456 (December 15, 1948); Chem. Abstracts **43,** 5032 (1949).
(43) JAEGER: U. S. patent 1,900,648 (March 7, 1933).

(44) Jaeger: U. S. patent 1,909,354–5 (May 16, 1933).
(45) Kosmin and Emerson: U. S. patent 2,447,414 (August 17, 1948).
(46) Krieble and Denton: U. S. patent 2,440,233–4 (April 20, 1948).
(47) Law and Chitwood: U. S. patent 2,279,469–70 (April 14, 1942).
(48) Loder: U. S. patent 2,223,493 (December 3, 1940).
(49) Loder: U. S. patent 2,223,494 (December 3, 1940).
(50) McNamee and Dunn: U. S. patent 2,339,346–8 (January 18, 1944).
(51) Rust and Bell: U. S. patent 2,380,675 (July 31, 1945).
(52) Rust, Raley, and Vaughan: U. S. patent 2,421,392 (June 3, 1947).
(53) Rust and Vaughan: U. S. patent 2,369,181–2 (February 13, 1945).
(54) Vaughan and Rust: U. S. patent 2,395,523 (February 26, 1946).