Mechanism of the Reactions of Oxygen With Fatty Materials. Advances From 1941 Through 1946[1]

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Introduction

THE mechanism of oxidation of fatty materials with air or oxygen is of considerable industrial as well as theoretical importance, and its attempted understanding has been the subject of many scientific investigations for about 100 years (9, 12, 41). With a few noteworthy exceptions research prior to 1941 was conducted on the oils themselves, and most of the work was concerned with measuring the change in properties of the oil as oxygen was absorbed. Since glyceride oils are extremely complex, it was usually impossible to explain the numerous phenomena that occurred simultaneously. To complicate the situation still further, the analytical methods employed, although usually satisfactory for unoxidized oils, were frequently unreliable when applied to oils containing oxidized and polymerized products.

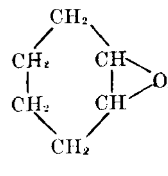
Within the past decade, several groups of workers, both in this country and abroad, realizing that comparatively little was known about the oxygen oxidation of fatty materials in spite of the voluminous literature on the subject, have studied the oxidation of purified fatty materials of known structure derivable from fats and oils, or the oxidation of simple, pure compounds having structures closely related to those found in fats and oils. By attacking the problem in this way, these workers have laid a foundation for explaining the numerous reactions which take place when an oil "dries" or when oxidative rancidity occurs. They have been concerned, to a great extent, with the primary products of oxidation, especially the peroxides initially formed, and have also fractionated the oxidation products in an attempt to isolate pure compounds or mixtures less complex than the oxidation products. A physical chemical approach has also been employed in many instances in an attempt to obtain much needed thermal and kinetic data. Fortunately, such tools as chromatographic adsorption, molecular distillation, ultra-violet spectrophotometry, and low-temperature fractional crystallization have been available to recent investigators, and much information which the earlier investigators were unable to get is now easily obtainable. As a result of this more fundamental approach to the problem and the availability of modern tools, more progress has probably been made in clarifying the mechanism of oxygen oxidation of glyceride oils in the past five years than in the entire previous history of the subject. It should be emphasized at the outset, however, that the subject is not completely understood and much information must be obtained before the correct mechanisms can be established.

The purpose of the present article is to discuss briefly the more important advances made mainly from 1941 through 1946 in the chemistry of the mechism of the oxygen oxidation of fatty materials and related substances. The last review article on this subject in the American literature covered the period through 1940 (55), and the various standard reference works which contain information on oxygen oxidation were published prior to 1939 (11, 37, 45).

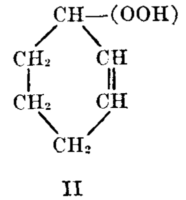
[The supplementary list of papers, most of which were published to 1941, will give readers a background of the knowledge of the oxidation of glyceride oils and related materials with oxygen since 1820. These papers are not referred to in the manuscript.]

Monounsaturated Compounds

Much information regarding the mechanism of oxygen oxidation of monounsaturated compounds derived from fats and oils has been obtained by studying the oxidation of simple, monounsaturated, non-fatty compounds, such as cyclohexene, which can be prepared readily in a high degree of purity. In 1928 Stephens (46) reported the isolation of a peroxide of cyclohexene, $C_6H_{10}O_2$, which he obtained by treating cyclohexene with oxygen in daylight, and he assumed, on the basis of the theories of oxidation accepted at that time, that the product was saturated (I). Further research, however, by Criegee, Pilz, and Flygare (10), Hock (31), and notably, by Farmer and Sundralingam (19), established the fact that Stephens' product was a hydroperoxide and that a double bond was present (II). It was also determined by the British workers that 1-methyl-1-cyclohexene and 1,2-dimethyl-1-cyclohexene behave similarly when oxidized with oxygen (19). The actual isolation of purified hydroperoxides from oxidized olefins was a tremendous step forward, and it cast much doubt on the validity of the Engler (14) and Willstätter and Sonnenfeld (56) concepts of olefin oxidation.



I



II

In a logical extension of the earlier work on pure monoolefins of relatively low molecular weight, Farmer and Sutton (22) prepared methyl oleate hydroperoxide by oxidizing purified methyl oleate with oxygen while irradiating the reaction mixture

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[1] Presented at the meeting of the American Oil Chemists' Society, held in Chicago, Ill., on October 21, 1947.

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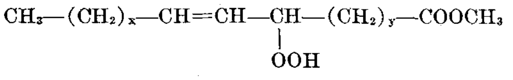
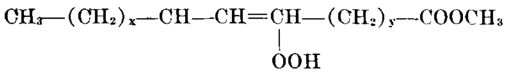
with ultra-violet light. Purified methyl oleate hydroperoxide (III and IV) was isolated by molecular



$$CH_3\text{—}(CH_2)_x\text{—}CH{=}CH\text{—}\underset{\underset{\displaystyle OOH}{|}}{CH}\text{—}(CH_2)_y\text{—}COOCH_3$$

III



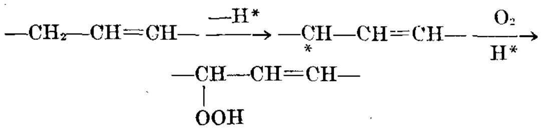
$$CH_3\text{—}(CH_2)_x\text{—}CH\text{—}CH{=}\underset{\underset{\displaystyle OOH}{|}}{CH}\text{—}(CH_2)_y\text{—}COOCH_3$$

$(x+y=13)$

IV

distillation and also by chromatographic adsorption. The hydroperoxide was shown to contain about the theoretical peroxide oxygen content and, by hydrogenation and iodine value determination, to have a double bond. The position of the double bond is not known with certainty, and in all likelihood it is not in the original position (24, 29). Subsequently, in a study of oxidation kinetics, Bolland and Gee (4, 5) showed that the hydroperoxide formed in substantially quantitative yield during the early stages of oxidation. Sutton (48) studied the air oxidation of methyl elaidate and although he did not isolate the hydroperoxide, he showed that during the early stages of the reaction substantially all the absorbed oxygen was peroxidic and that the double bond was affected to a limited extent only. Recently, Swift, Dollear, and O'Connor (52) described an excellent method for preparing methyl oleate hydroperoxide by the reaction of pure methyl oleate with oxygen in the presence of ultra-violet light, followed by low-temperature fractional crystallization of the oxidation products from acetone. These workers also studied reactions of the hydroperoxide.

Hydroperoxide formation occurs readily under mild reaction conditions in non-ionizing solvents and appears to be substantially autocatalytic and independent of oxygen pressure (16, 30). It appears to follow a free-radical mechanism sometimes depicted as shown below:

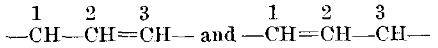


$$\text{—}CH_2\text{—}CH{=}CH\text{—}\xrightarrow{-H^*}\text{—}\underset{*}{CH}\text{—}CH{=}CH\text{—}\xrightarrow[H^*]{O_2}\text{—}\underset{\underset{\displaystyle OOH}{|}}{CH}\text{—}CH{=}CH\text{—}$$

The ease with which hydroperoxides are formed has prompted many investigators to assume that they must be the initial products of oxidation, but it is difficult to explain their formation by such a simple equation since the separation of an α-methylenic hydrogen atom requires about 80 k. cal. of energy, which must be supplied in some manner. It is known, however, that all conjugated compounds (discussed later) which have been investigated, including those containing α-methylene groups, peroxidize by adding oxygen at the double bonds, leaving the α-methylene groups intact. Farmer has pointed out (15, 16), therefore, that since molecular oxygen is able to begin its attack at a double bond, presumably by adding at one end of it, and since the high expenditure of energy required at the beginning of the reaction for the dissociation of the C-H bond would be considerably diminished if oxygen were to begin its attack *additively* in only a few of the molecules, and thereafter to continue the attack *substitutively by means of chain reactions* involving free radicals, there is good justification for postulating *universal initiation* of autoxidative attack in olefins by addition at the double bond. Therefore, the α-methylene reaction, characteristic of unconjugated olefins, may proceed as shown in the two-column equation.

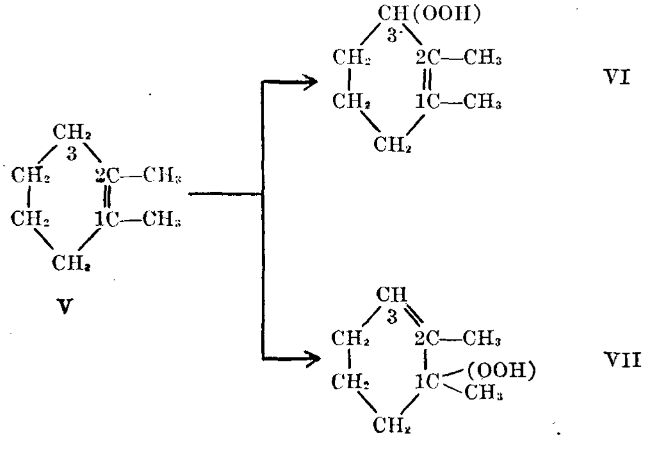
That oxygen molecules initially attack the double bond in methyl oleate has also been suggested by Gunstone and Hilditch (29). A reaction scheme such as the one shown is completely satisfactory kinetically (5) and thermochemically (6). It should be emphasized that, although actual addition of oxygen at the double bonds at the start of the reaction is relatively insignificant in terms of total oxygen absorbed, it is sufficient to initiate the necessary chain reactions (15, 16).

If the free radical mechanism is correct, resonance between the three-carbon systems



$$\text{—}\underset{*}{\overset{1}{CH}}\text{—}\overset{2}{CH}{=}\overset{3}{CH}\text{—}\ \text{and}\ \text{—}\overset{1}{CH}{=}\overset{2}{CH}\text{—}\underset{*}{\overset{3}{CH}}\text{—}$$

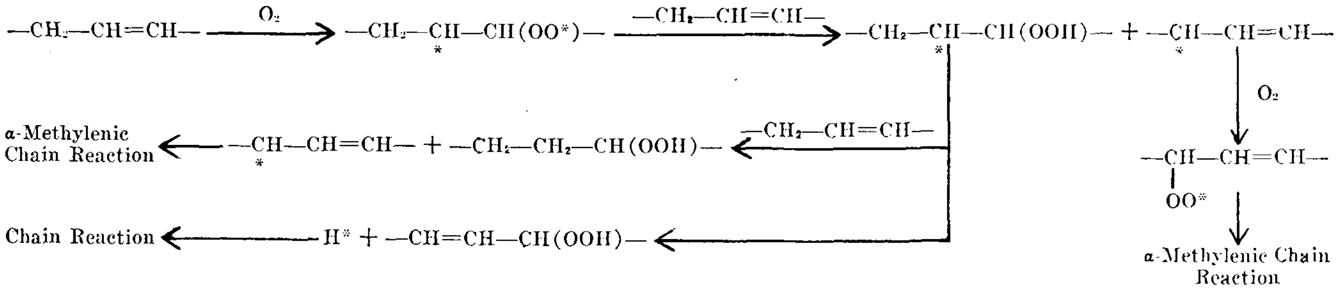
will occur (18) and when a molecule of oxygen and an atom of hydrogen are incorporated into the oxidizing molecule, there should be an approximately equal tendency for the hydroperoxide group to appear at positions 1 and 3, thus fixing some of the double bonds in the original position and the remainder at the adjacent pair of carbon atoms. This shift of the double bond, which had been demonstrated spectrophotometrically by Farmer, Koch, and Sutton (18) in the case of polyunsaturated compounds (discussed later), was suggested by them for monoolefins, although no experimental evidence was offered. Evidence for this conclusion was recently obtained by Swern, Knight, Scanlan, and Ault (50), who studied the air oxidation of purified methyl oleate. These investigators concluded, on the basis of oxidative splitting of certain of the oxygenated fractions, that a double bond shift must have occurred during oxidation. Additional chemical evidence that a double bond shift occurs in monoolefin oxidations and, therefore, that a free-radical mechanism is probably applicable in these and comparable oxidations, was recently obtained by Farmer and Sutton (24). They studied the oxidation of 1,2-dimethyl-1-cyclohexene (V) and concluded that both 1,2-dimethyl-1-cyclohexene-3-hydroperoxide (VI) and 1,2-dimethyl-2-cyclohexene-1-hydroperoxide (VII) must have formed:



V

VI

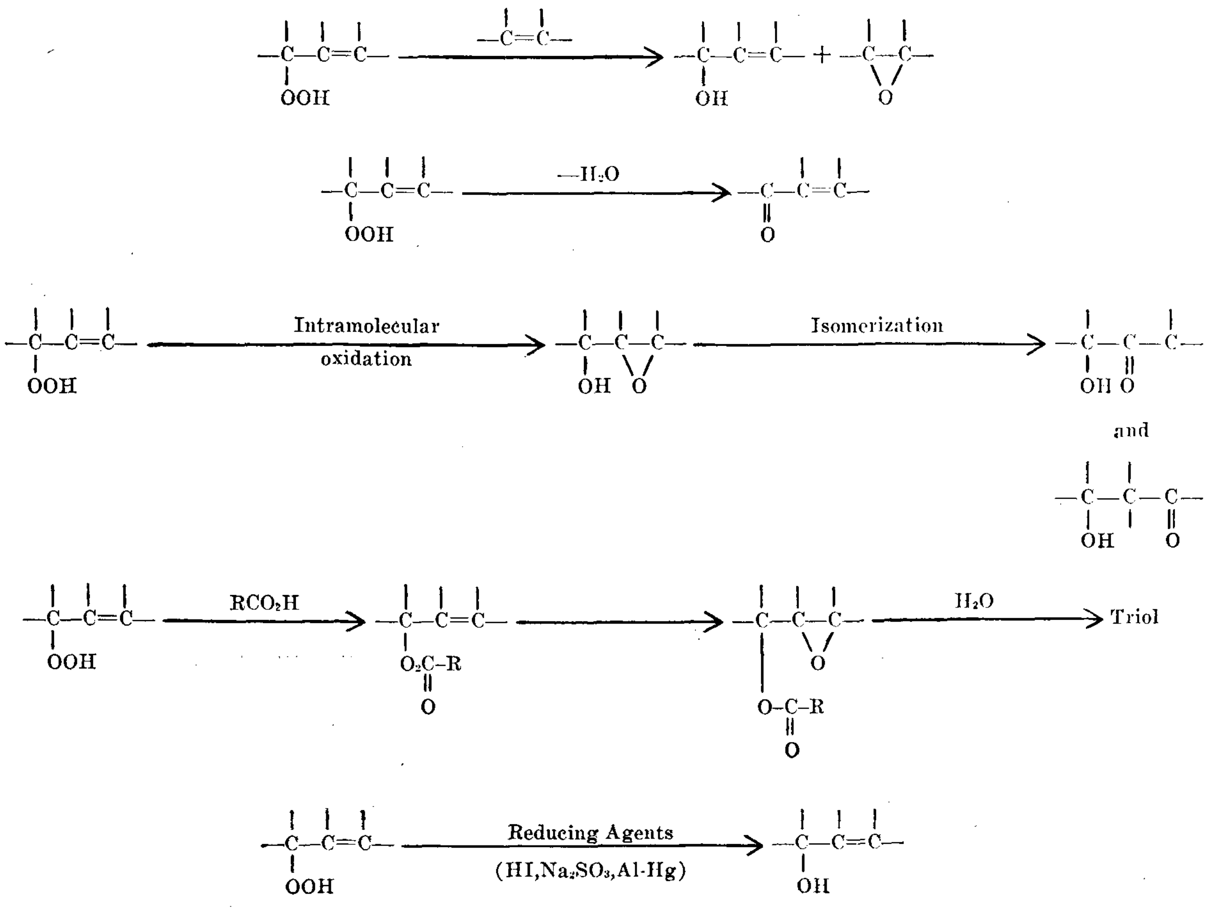
VII

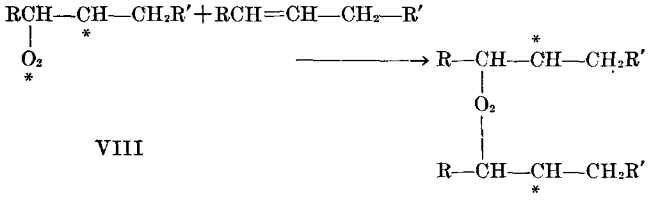


Recently, Atherton and Hilditch (1) and Gunstone and Hilditch (28) compared the oxygen oxidation of purified methyl oleate at 20° and at higher temperatures, and concluded that at the lower temperature peroxidation occurs to a large extent at the methylene groups adjacent to the double bond whereas at the higher temperature oxygen appears to combine directly with the double bond.

After peroxides form, the order in which numerous oxidation and polymerization products form is not known. Several investigators have studied the chemical reactions of pure hydroperoxides (10, 17, 19, 31, 44), but the way in which they react in oxidation mixtures is still a mystery. Some of the reactions of pure olefin hydroperoxides are shown at the bottom of the page.

Although most of the recent research on monoolefin oxidations has been directed toward explaining the early stages of the reaction and accounting for the initial products of oxidation, various workers have studied the polymeric portion which frequently represents the major proportion of the total oxidation products. Recently, Powers, Overholt, and Elm (43) concluded that oxidation polymers are formed by a mechanism of the vinyl type and, therefore, that they are linked by carbon-to-carbon bonds. This conclusion was based primarily on analytical determinations on the unfractionated oxidation mixture. Swern, Knight, Scanlan, and Ault (50), however, fractionated, by molecular distillation, the polymers obtained during the catalytic air oxidation of methyl oleate and concluded that the polymers are probably linked by some type of ether-oxygen bond. That oxidation polymers may be linked by oxygen atoms has also been suggested by other workers (13, 27, 38) although the evidence for such a conclusion was often not apparent. Recently, Farmer (16), Farmer and Sundralingam (19), and Bolland and Gee (6) have proposed possible mechanisms for the formation of oxygen-linked polymers. Perhaps the best information on the subject is that of Bolland and Gee, who have postulated that oxygen-linked polymers may form by the reaction of radical VIII with unreacted olefin. These





$$\underset{\underset{*}{O_2}}{\overset{}{\underset{|}{RCH}}}—\underset{*}{CH}—CH_2R' + RCH{=}CH—CH_2—R' \longrightarrow \begin{array}{l} R—CH—\overset{*}{CH}—CH_2R' \\ \quad\;\; | \\ \quad\;\; O_2 \\ \quad\;\; | \\ R—CH—\underset{*}{CH}—CH_2R' \end{array}$$

VIII

free-radical ends could react further with oxygen, producing peroxide radicals, which could again add olefin, thus building up a polymeric chain in which the repeating unit is $^*CH—(CH_2R')—CHRO_2{}^*$. That some type of recurring unit is formed was shown by Swern, Knight, Scanlan, and Ault (50), who pointed out that the saponification equivalent and specific refraction of methyl oleate oxidation polymers were substantially constant, thus indicating that a recurring molecular unit was probably the building block of the polymers. The formation of carbon-to-carbon linked polymers, however, is also thermochemically possible and must be considered, especially at low oxygen pressures (6). Other modes of formation of oxygen-linked polymers are the reaction of compounds containing hydroxyl groups with those containing oxirane groups (both of which are present in air oxidation mixtures), the reaction of a hydroperoxide with an olefin yielding mainly dimers (17), and the interaction of the numerous radical forms of the type RO*, ROO*, and R* with various components of the oxidation mixture (17). The actual mechanism by which polymers form is still unknown, but it was concluded by Swern, Knight, and Scanlan (51) that polymer formation probably does *not* occur as a result of the interaction of oxirane groups with hydroxyl groups.

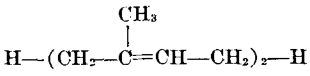
The point at which polymers form and their exact role in air oxidation are also not known. The fact that many fatty materials give a high yield of polymer and that the polymers often display syneresis suggests that they are formed early in the oxidation (53) and that chain scission products result from oxidative splitting of the polymer. We have studied the mild, air oxidation of the polymers obtained in the air oxidation of methyl oleate and observed that short-chain, scission products form with great ease (35). Although this does not prove that scission products form from the polymer, such a possibility must be given serious consideration.

In view of the uncertainty regarding the order in which the various oxidation products, as well as their precursors, form, we have not attempted to propose a general reaction scheme to account for the numerous oxidation and polymerization products. The best such scheme is that of Hollis (32). However, he makes no reference to polymer formation.

Polyunsaturated Compounds

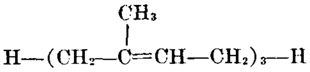
Nonconjugated Compounds. Nonconjugated polyunsaturated compounds may be divided into two groups, namely, those with 1,4-unsaturation, and those with more widely separated double bonds. The latter group is not considered separately, since such compounds behave like monoolefins, which have already been discussed.

The oxidation of the polyunsaturated hydrocarbons, dihydromyrcene (IX), dihydrofarnesene (X), and squalene (XI), was studied by Farmer and Sutton (21), who showed that during the early stages of



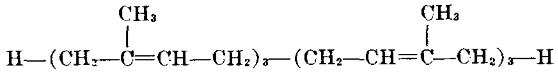
$$H—(CH_2—\overset{\overset{CH_3}{|}}{C}{=}CH—CH_2)_2—H$$

IX



$$H—(CH_2—\overset{\overset{CH_3}{|}}{C}{=}CH—CH_2)_3—H$$

X

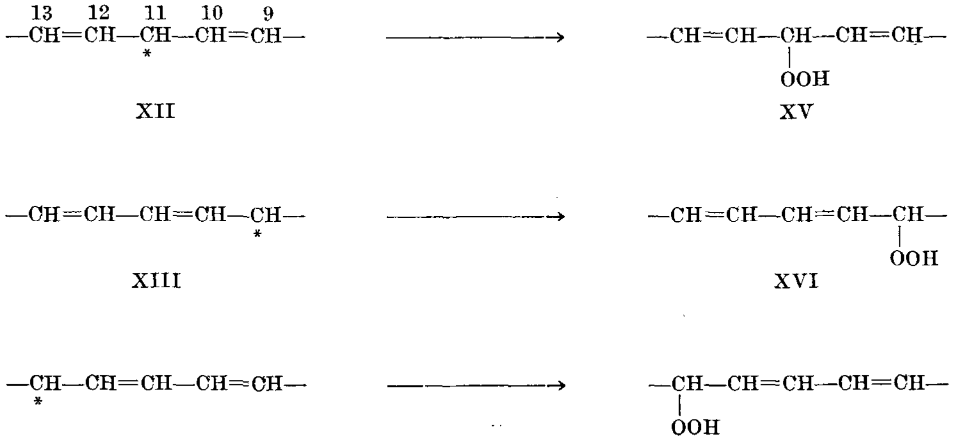


$$H—(CH_2—\overset{\overset{CH_3}{|}}{C}{=}CH—CH_2)_3—(CH_2—CH{=}\overset{\overset{CH_3}{|}}{C}—CH_2)_3—H$$

XI

oxidation substantially all the absorbed oxygen was in the form of hydroperoxides and that the original unsaturation of the compounds was unaffected. This work on nonconjugated polyolefins was extended by numerous other investigators (2, 3, 4, 7, 15, 18, 20, 23, 33, 49, 54) to include ethyl linoleate and linolenate, methyl docosahexaenoate, rubber, and other compounds, and the general conclusions regarding hydroperoxide formation discussed earlier in this paper were confirmed.

In the oxidation of ethyl linoleate (7) the monohydroperoxide which forms was shown by ultra-violet absorption measurements to contain approximately 70% of conjugated diene isomers. On the basis of the free radical mechanism, oxidative attack at the active



$$\overset{13}{—CH}{=}\overset{12}{CH}—\underset{*}{\overset{11}{CH}}—\overset{10}{CH}{=}\overset{9}{CH}— \longrightarrow —CH{=}CH—\underset{\underset{OOH}{|}}{CH}—CH{=}CH—$$

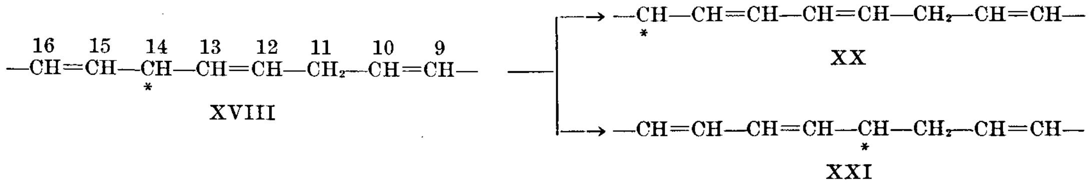
XII XV

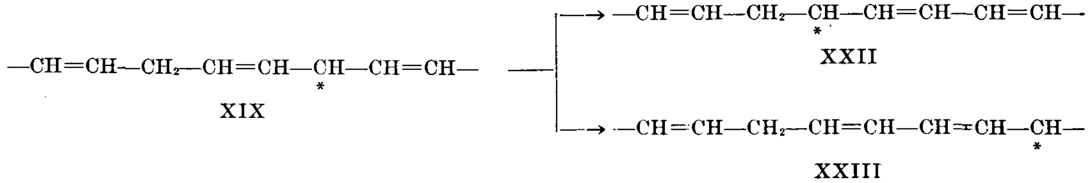
$$—CH{=}CH—CH{=}CH—\underset{*}{CH}— \longrightarrow —CH{=}CH—CH{=}CH—\underset{\underset{OOH}{|}}{CH}—$$

XIII XVI

$$—\underset{*}{CH}—CH{=}CH—CH{=}CH— \longrightarrow —\underset{\underset{OOH}{|}}{CH}—CH{=}CH—CH{=}CH—$$

XIV XVII





methylene group at C_{11} (not the initial point of entry of oxygen—see earlier discussion) would result in the formation of a free radical which is a resonance hybrid of the three equivalent structures, XII, XIII, and XIV, and the hydroperoxides derived from them would then be expected to contain the three isomeric forms, XV, XVI, and XVII. Bergstrom (2), however failed to isolate the anticipated 11-hydroxystearic acid when methyl linoleate oxidation products were hydrogenated, although the 9- and 13-hydroxystearic acids were obtained. This is hardly adequate evidence for assuming the absence of an 11-hydroperoxide, in view of the known difficulties in separating, purifying, and distinguishing between the isomeric monohydroxystearic acids. An alternative explanation for the failure to isolate 11-hydroxystearic acid has been suggested by Jones (34), who proposed a conjugative isomerization during catalytic reduction. If the three hydroperoxides are produced in equal amounts, 67% of conjugation will result although up to 100% can conceivably occur if the two conjugated forms are favored. The formation of free radicals in this oxidation and the further progress of the reaction by a chain reaction mechanism, similar to that proposed earlier for monoolefins, is both kinetically and thermally reasonable (5, 6).

In the case of ethyl linolenate (18) there should be two initial radical forms (XVIII and XIX) which could rearrange to XX, XXI, XXII, and XXIII. The hydroperoxides derived from XX through XXIII would then show diene conjugation. If both the active methylene groups were attacked consecutively by oxygen, which would happen frequently only in advanced stages of oxidation, then numerous diperoxide forms would become possible, some of which would show diene conjugation, some triene conjugation, and one the original state of unconjugation. Ultra-violet absorption spectra show that after the incorporation of one mole of oxygen per mole of ethyl linolenate rearrangement of double bonds has progressed to a stage at which about 21.0% of the ester contains two double bonds in conjugation and 3.5% has all three double bonds conjugated.[3]

Methyl docosahexaenoate (18, 23), which is an extremely complex substance, also displays an increased absorption in the ultra-violet region, indicating that conjugated compounds are formed, but no quantitative data have been reported on this material.

In those olefins in which an active $-CH_2-$ group (or groups) is surrounded by double bonds, the rate of uptake of oxygen is increased tremendously over that of simple monoolefins. Thus, Stirton, Turer, and Riemenschneider (47) showed that the rate of oxygen absorption of pure methyl oleate, methyl linoleate, and methyl linolenate was in the proportion of about 1:10:16, and Gunstone and Hilditch (28), in a similar investigation, showed that the relationship was about 1:12:25. Quantitative data of this type serve to confirm the hydroperoxide theory further since, if oxygen added to double bonds exclusively, as has been proposed by many earlier workers, the relationship just described should be closer to 1:2:3.

In the case of squalene and rubber (18) no large increase in ultra-violet absorption which could be ascribed to the formation of conjugated units was observed. In these materials the reactive α-methylene groups are flanked on only one side by a double bond. This leads to a much lower reactivity of the olefin and requires two peroxidations to occur in any diene unit of the chain, $-C{=}C-C-C-C{=}C$, before conjugation can appear. Since the hydroperoxide group in these compounds is very unstable, it is not surprising that peroxidation does not produce conjugation. There is little doubt, however, that double-bond migration is occurring. It is unfortunate that the ultra-violet absorption technique is inapplicable to such systems.

No detailed study of the polymers obtained in the air oxidation of nonconjugated polyunsaturated compounds has been reported. The fact that a large proportion of conjugated substances are formed (7, 18), however, suggests that carbon-to-carbon linked polymers may be produced as a result of a peroxide-catalyzed reaction. This is in line with the view of Powers, Overholt, and Elm (43). It is the present authors' opinion that the polymers obtained in the air oxidation of linoleates and linolenates probably consist of a mixture of carbon-to-carbon and oxygen-linked compounds.

A detailed reaction scheme of the oxidation of linoleic esters is given by Hollis (32). Unfortunately so little is known about polyunsaturated compounds that much of this is highly conjectural. Franke and Mönch (25) have questioned the validity of the hydroperoxide theory in the oxidation of linoleic and linolenic acids on the basis of their experimental work in which a cobalt catalyst was employed. Although they appear to have performed a careful piece of work,

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[3] Farmer, Koch, and Sutton (18), however, reported 28.5% and 4.5% diene and triene conjugation, respectively. These values have been recalculated, employing standardization data for pure conjugated acids (7) [Brice and Swain, J. Optical Soc. Am. *35*, 532 (1945)].

they apparently did not or were unable to study the extremely early products of oxidation, as Farmer and his co-workers did. We believe that their results can also be interpreted in accordance with the hydroperoxide theory of olefin oxidation.

Conjugated Compounds. Recent studies in the air oxidation of conjugated olefins have been reported by Farmer (15, 16), Holman and co-workers (33), and Brauer and Steadman (8). Farmer has pointed out that all peroxides of non-aromatic conjugated dienes and polyenes (both open-chain or cyclic) studied so far form rapidly in ultra-violet light or slowly in diffused light and are produced by addition of oxygen at the diene systems. Even if the conjugated system is flanked on one or both sides by methylene groups, as in methyl sorbate and methyl eleostearate, the reaction is still restricted to addition of the double bond systems. The peroxides which form show high thermal stability, and they are polymeric substances which rarely exceed octameric complexity and contain little or no monomeric component. Not only do these peroxides show high thermal stability, but they undergo chemical reduction and catalytic hydrogenation incompletely. The structure of these polymeric peroxides is not known, but Farmer has suggested some possibilities on the assumption that 1:4 addition of oxygen occurs primarily. On catalytic hydrogenation the polymeric peroxide of methyl eleostearate gives at least a 60% yield of mixed hydroxyketostearic and dihydroxystearic acids. Polymeric cyclohexadiene peroxide gives both cis- and trans-1,4-dihydroxycyclohexene. Polymeric α-terpinene peroxide on half hydrogenation yields a corresponding 1,4-dihydroxymenthene. In neither case has the corresponding 1,4-ketol been recognized. Moderate yields of the 1,4-diol can be obtained from ascaridol.

The crude polymeric peroxides from open-chain conjugated systems usually contain up to 20% of oxidation scission products, which may form spontaneously during the absorption of oxygen or they may form in the presence of metallic catalysts during attempted catalytic hydrogenation of the peroxides. Oxidized methyl sorbate, 1,4-diphenylbutadiene, and probably methyl eleostearate are examples of products which undergo spontaneous scission and oxidized 2,3-dimethylbutadiene is an example of the catalyzed type. The spontaneous scission at individual double bonds occurs side by side with the terminal peroxidation of the conjugated diene units. Its occurrence may be interpreted either as evidence that a corresponding degree of 1,2- (or 3,4-) peroxidation accompanies the predominant 1,4-peroxidation, or as being due merely to some of the decomposing 1,4-peroxide molecules (thermally and catalytically activated) acting at random as an oxidizing agent for some of the surrounding unoxidized double bonds.

Brauer and Steadman (8) have studied the autoxidation of β-eleostearic acid and have followed the course and kinetics of the reaction spectrophotometrically. They showed that during the reaction a conjugated diene is formed which in turn is autoxidized. In order to destroy one mole of β-eleostearic acid, slightly less than one-half mole of oxygen is initially required. They have assumed, therefore, that the initial uptake of oxygen by β-eleostearic acid results in a dimerization involving the formation of some carbon-to-carbon bonds and that a polymerization reaction is induced by the peroxides formed in the course of the reaction.

The formation of carbon-to-carbon linked polymers by peroxide catalysis during the early stages of oxidation is extremely probable in compounds which are completely conjugated at the start. The decrease in refractive index which has been observed during the early stages of air oxidation of methyl eleostearate when the percentage of oxygen absorbed is low, coupled with the rapid increase in viscosity and molecular weight (42), may be interpreted to mean that the conjugated system is disappearing as a result of rapid carbon-to-carbon polymerization. If oxygen-linked polymers are formed during the early stages of oxidation, an increase in refractive index might be expected. Thus, the oxygen-linked polymers obtained in the air oxidation of methyl oleate have a much higher refractive index than methyl oleate itself (50). Furthermore, in the case of conjugated compounds, it is highly probable that non-peroxidic, oxygen-linked polymers form during the later stages of air oxidation (39).

Much fundamental work on the oxidation of eleostearic acid was published prior to 1941 by Morrell and his co-workers (40) and, therefore, is not discussed in this review.

Saturated Compounds

Under the mild conditions usually associated with the "drying" of an oil, long-chain saturated compounds have often been assumed to be inert. However, Stirton, Turer, and Riemenschneider (47) have shown that at 100°C. the ratio of rate of oxygen absorption of methyl stearate:methyl oleate:methyl linoleate:methyl linolenate is about 1:11:114:179. Also, in an investigation of the rate of oxidation of many hydrocarbons Larson, Thorpe, and Armfield (36) showed that at 110°C. n-decane and n-hexadecane absorb oxygen slowly during the early stages of oxidation (the first 20 hours), and then an autocatalytic acceleration to a constant rate, which is not insignificant, occurs. It can probably be concluded, therefore, that during the early stages of the "drying" process the saturated components of the oil play little or no part in the reactions but that as oxygenated components accumulate, particularly peroxides, the rate of reaction of long-chain saturated compounds begins to be significant. In fact, the oxidation of the saturated components of an oil may play an important role in the deterioration of paint films and similar coating materials.

On the basis of research conducted on saturated compounds, it has been concluded (26, 57) that hydroperoxides are the primary intermediates in their oxidation, the reaction proceeding by a chain mechanism and the hydroperoxides being converted mainly to ketones and alcohols with the ketones predominating.

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Summary

A review of advances from 1941 through 1946 in the mechanism of the oxygen oxidation of fatty materials is given. Subjects discussed are the oxidation of monounsaturated compounds, nonconjugated and conjugated polyunsaturated compounds, and saturated compounds.

The hydroperoxide theory of oxidation at active methylene groups is discussed in detail. There is good justification for postulating that autoxidative attack in olefins is *initiated* universally by addition of oxygen at the double bonds in only a *few* of the molecules, and not by the formation of hydroperoxides. Subsequently, in the case of monoolefins and nonconjugated polyolefins, the attack by oxygen is continued by *substitution* on the α-methylene group to form hydroperoxides by means of *chain reactions.* Mechanisms for such an oxidative scheme, involving the formation of intermediate free radicals, are given. In the case of conjugated compounds, peroxides are formed by addition of oxygen at the double bonds, and α-methylene group peroxidation does not occur. Although saturated compounds are relatively inert, they also form hydroperoxides, which are converted mainly to ketones and alcohols with the ketones predominating.

The formation of polymers, which often account for the major proportion of the oxidation products of unsaturated compounds, also is discussed. The possibility of formation of carbon-to-carbon-linked as well as oxygen-linked polymers in the various classes of olefins is considered.

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Developments in the Refining of Oils With Sodium Carbonate

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SEVERAL years have elapsed since the writer described the Clayton Soda Ash Refining Process (1). The purpose of this paper is to review some of the developments that have since been made in refining fatty oils with sodium carbonate. The desirable properties that sodium carbonate has of neutralizing the free fatty acids without appreciable attack on the triglycerides under refining temperatures and the relatively low cost of this chemical were well known. But the evolution of carbon dioxide from the reaction of sodium carbonate with the free fatty acids resulted in persistent emulsions and floating soapstock. A method that would successfully employ sodium carbonate for refining oil with separation into clean oil and low free oil soapstock remained a challenge. It was not until the Clayton process in which the dehydration-rehydration sequence was employed that the problem may be said to have been solved in a practical manner. It is not within the scope of this paper to go into details of equipment for carrying out the process or to refer to and describe the layout of installations that have been made. The discussion will be confined to certain chemical aspects of the refining at different stages. The process, as carried out in practice is stream lined and continuous. Units of one- to four-tankcar a day capacity have been in operation for the past few years. The essential components of the process will be described in condensed fashion. A complete account of it has been published (1).

The neutralizing sodium carbonate solution 20°Bé. in excess, usually 1.5 times that required to combine with the free fatty acids, is added to the flow of crude oil. The mixture is heated to 190-212°F. before it is introduced into a vessel, a dehydrator, maintained under a vacuum, where the water is flashed off and any gases released. With crudes of a high per cent of gums or a high ratio of gums to F.F.A., a larger excess of sodium carbonate is recommended. The oil and dehydrated soapstock are pumped from the dehydrator and rehydrated with sodium carbonate solution. The amount employed on the average will vary from 2 to 7% of a 20°Bé. solution with the most common 3 to 4%. The sodium carbonate does not attack the oil to a measurable extent under these conditions and because of the high concentration of electrolyte prevents the formation of stable emulsions. Separation of the soapstock from the oil takes place readily in the centrifugal. The degree of fluidity of the discharging soapstock may be controlled and regulated by adjusting the amount of rehydration solution added. It is found advisable in most cases to maintain the soapstock at a level of 33 to 35% water, which is close to that of the water content of neat soap.

The sodium carbonate solution may be added in two streams for rehydration, one 20°Bé. injected into the dehydrated soapstock-oil mixture as it leaves the dehydrator, and the other, 12°Bé. to the soapstock in the centrifugal. In this way, for certain oils high in gums, some economy in sodium carbonate consumption may be effected. The first sodium carbonate solution for rehydration is added in an amount not quite sufficient to cause the soapstock to slide out of the centrifugal and be discharged readily. The second stream is regulated to that quantity that will result in the the uniform discharge of the soapstock. One of the important points in this type of operation is to have the sodium carbonate stream to the centrifugal below a given concentration, i.e., specific gravity, otherwise uneven discharge of the effluents occurs. Some soapstock begins to come over with the oil. This hap-