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POLYMERIZATION OF DRYING OILS

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I. INTRODUCTION

The hardening of drying oils is generally considered to be due to the action of oxygen and results in the oils being changed to hard, dry, resinous materials. In general, the primary reactions to be considered are the formation of unsaturated ester hydroperoxides, the decomposition of these materials, and their subsequent cross linking. The situation is somewhat complicated by the fact that these reactions, as well as others, can all occur simultaneously, and that the products are not easily isolated. For the purpose of simplicity, the examples presented in the body of this report are usually pure compounds. However, it should be understood that the drying oils in general are mixed glyceryl esters of oleic, linoleic, linolenic, and eleostearic acids, as well as related saturated and unsaturated acids, and the examples are taken from these materials.

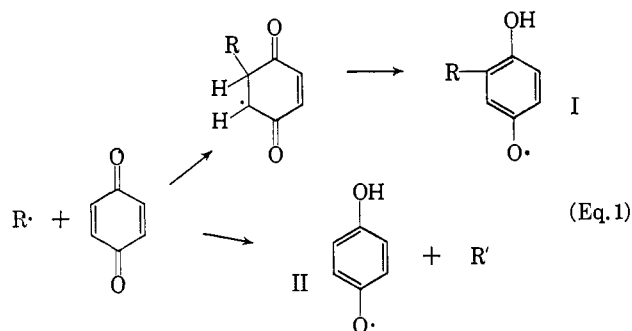
More details on the subject of autoxidation, and other topics pertinent to the polymerization of drying oils, are given in various reviews of these fields (8, 22, 44, 61, 83, 110, 112, 115, 122, 133, 147, 155, 156, 161, 182).

II. POLYMERIZATION INITIATION AND PEROXIDE FORMATION

A. INHIBITION

The initiation of the oxidative chain reaction, which is primarily responsible for the drying of natural oils, is often preceded by an induction period. This has been attributed to the presence of natural antioxidants such as the tocopherols. These naturally occurring

phenols can undergo an oxidation-reduction cycle in a manner similar to that of hydroquinone or act as inhibitors in the same fashion as phenols.

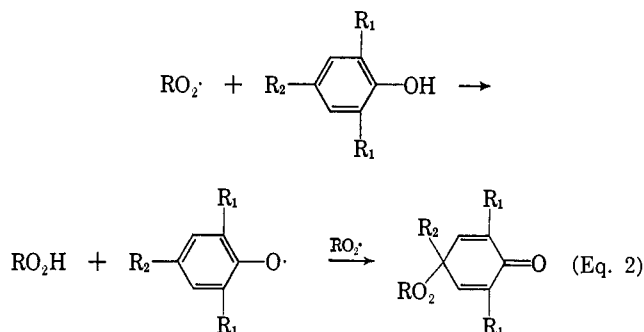


The activity of quinones in destroying radicals and terminating radical reactions is shown in Eq. 1 (39-41). Radicals I and II could then be oxidized back to their quinoid form to resume their activity as inhibitors.

Inhibitors such as amines and phenols (81, 82, 174, 175) can reduce the rate of decomposition of free radicals, and methyl linoleate has a short induction period in the presence of water (158).

It is believed that the effectiveness of trialkylphenols results from their ability to react with two peroxy free radicals according to Eq. 2.

The reaction products in Eq. 2 have been identified in the case where R_1 was *t*-butyl and R_2 was methyl (15, 33). In the cases where hydroquinone was used and the reaction was stopped at the point where only 1 mole of peroxide had interacted, the semiquinone radical



disproportionated to form equimolar amounts of quinone and hydroquinone (25). This reaction serves to illustrate a number of methods whereby the unoxidized phenols are useful in delaying oxidation reactions which are essential in the drying of oils. This type of antioxidant effect is illustrated in Fig. 1 (133).

The choice of specific oxidation inhibitors of these and other types can be aided by considering the oxidation-reduction potential as an indication of reducing or inhibiting power. A number of inhibitors have been classified based on their ability to prevent the drying of linseed oil, and the order could be correlated with the oxidation-reduction potential (in volts) (119): excellent, *p*-aminophenol (0.7405); good, pyrocatechol (0.810), *m*-aminophenol (0.962), diphenylamine (1.072), and 2-naphthol (1.0825); fair, 2-naphthylamine (1.132), phenol (1.1572), and aniline (1.204). Under ideal circumstances, of course, an antioxidant (A) should not

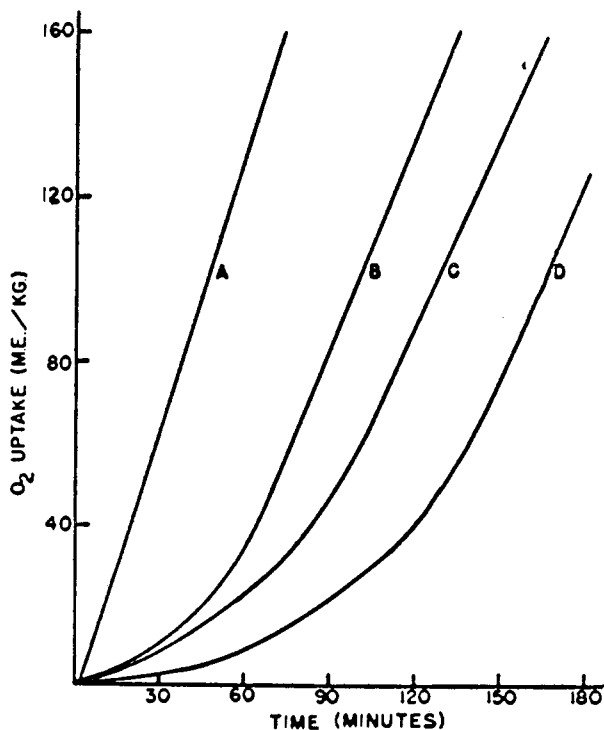
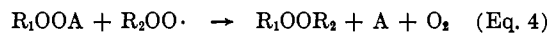
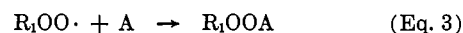


Fig. 1.—The autoxidation of methyl linoleate hydroperoxide at 30°: A, no antioxidant; B, 0.05% hydroquinone; C, 0.05% nordihydroguaiaretic acid; D, 0.05% propyl gallate (reprinted from ref. 133).

only react with the free radical and terminate this type of reaction, but should also be capable of further reaction with another free radical with the resulting regeneration of the original antioxidant (44).



The induction period, however, need not be considered to be due to the effect of inhibitors only. In certain cases, for example, an induction period is still observed even after rigorous purification of the starting materials by means of chromatography. In these cases, the induction period, *i.e.*, the period of time necessary for the initiation of oxygen absorption, may be an inherent property of the substance itself, and is an indication of the potential energy barrier in the chemical reaction scheme. This type of induction is well illustrated by the fact that when pure, freshly distilled fatty esters are examined for the onset of oxygen absorption, a definite time lag exists before this phenomenon is detected (134). This phase has not been fully explored, and hence there is a lack of definite detailed experimental evidence in this area. The effect of the two types of induction periods is clearly displayed and separated in Fig. 2, wherein the induction

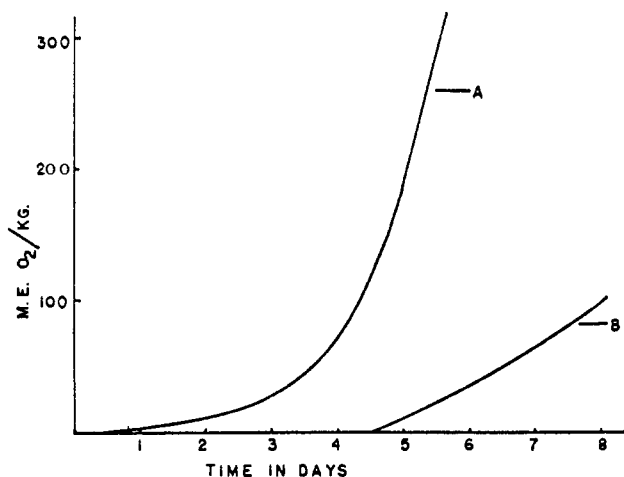


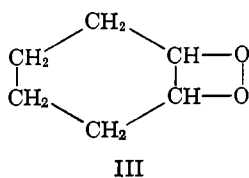
Fig. 2.—The autoxidation of methyl *cis*-9,*trans*-11-linoleate at 30°: A, no antioxidant; B, 0.1% nordihydroguaiaretic acid (reprinted from ref. 133).

period due to the necessity for overcoming the activation energy of the peroxide formation is shown in curve A, whereas the period necessary to overcome the inhibitor, nordihydroguaiaretic acid, is shown in curve B (133).

One method of eliminating the induction period is to add a small quantity of a hydroperoxide. For example, it has been shown that the addition of 1% of methyl linoleate hydroperoxide to pure methyl oleate eliminated the induction period completely (101). The same effect was shown when benzoyl peroxide was added to linseed oil (68).

B. PEROXIDE FORMATION

The autoxidation of simple unsaturated compounds, such as cyclohexene, was at first thought to consist of an initial attack on the double bonds of a particular system, and that the compounds isolated were peroxides which were cyclic in nature (159) as shown by structure III. Later work showed that the products



were noncyclic α -methylene hydroperoxides and that the double bonds were still intact (47, 58, 80). As an extension to drying oil chemistry, it was also shown that when purified methyl oleate was irradiated with ultraviolet light in the presence of oxygen, a hydroperoxide could be isolated (59).

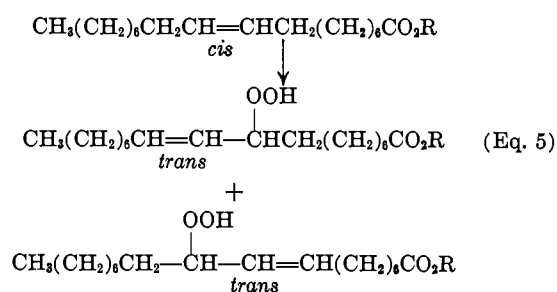
The isolation of the hydroperoxide from the gross reaction mixture has presented many problems. Various techniques have been developed which are useful with simple fatty acid esters. The successful use of these techniques has permitted careful analysis and identification of the oxidation products of drying oils and has done much to cast light on the chemical reactions involved in the drying process.

Early workers in the field obtained hydroperoxide concentrates by such methods as molecular distillation (59), low-temperature solvent crystallization (166), and absorption chromatography (13, 26, 52, 59). These techniques, however, often produce low yields of pure hydroperoxides owing to their decomposition during the varied isolation processes. More recently, purer hydroperoxide concentrates have been obtained by counter-current solvent distribution (34, 66, 67, 136, 192), by fractionation of canal complexes with urea (42), and by means of liquid partition chromatography (31, 63, 150).

If the extent of oxidation did not exceed 15–20%, the use of these techniques has permitted the isolation of hydroperoxide concentrates having a purity up to 90%.

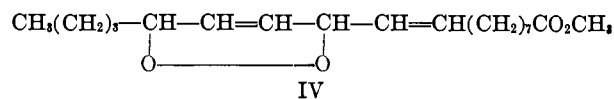
Manometric measurement of oxygen absorption of methyl oleate has shown that the first stable products were hydroperoxides. An early kinetic survey established that the hydroperoxides were formed in substantially quantitative yield during the primary stages of the autoxidation process (20, 23). It was also shown that the ethylenic bond was still intact and that no dimers were formed (67). The unsaturated linkage, although still intact, was shown to be transformed from the *cis* form to the *trans* geometric isomer (34, 103, 164), which is the more stable form. The detection of this

was accomplished by means of infrared spectroscopy. Because of the marked difference in stability, it has been proposed that the *cis* form of methyl oleate hydroperoxide has never been prepared by autoxidative techniques (162). In addition to the *cis* to *trans* isomerization, it has been shown that the double bond in methyl oleate is also displaced from its original 9-position to a different location (145). Degradative analysis techniques have shown that most of the resulting hydroperoxides are 9-hydroperoxido-*trans*-10-octadecenoate and 10-hydroperoxido-*trans*-8-octadecenoate, although it is also believed that other isomers, such as the 8- or 11-hydroperoxides, are also formed. The transformations of these materials are illustrated in Eq. 5. Although the peroxidic prod-



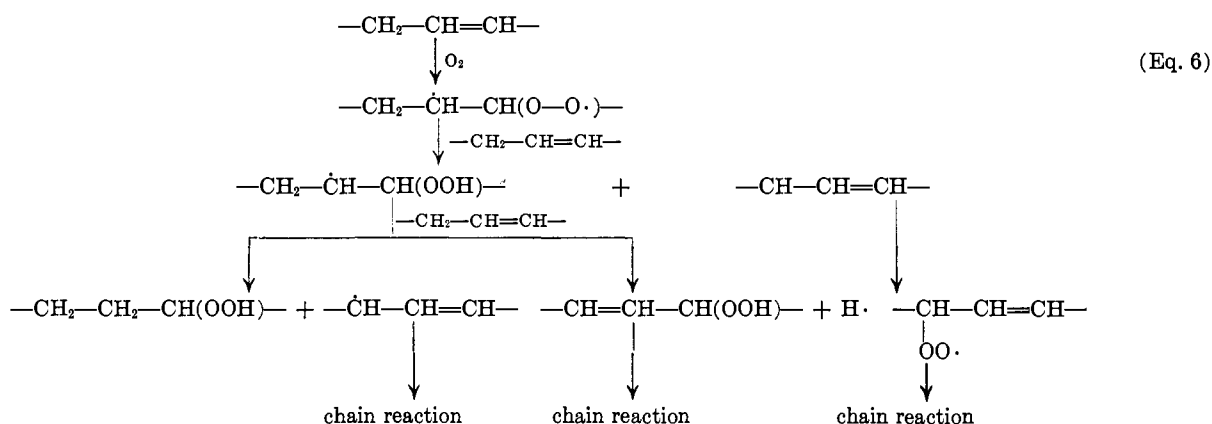
ucts of autoxidation which are mostly emphasized are the hydroperoxides, it is evident that they are not the sole products. By means of polarographic analysis, which permits the detection of hydroperoxides in the presence of other peroxides, it was shown that, in peroxide concentrates, as much as 28% of the peroxidic materials are other than hydroperoxides (162). The structures of the other materials have not been proved, but it is conceivable that they are the cyclic peroxides which were postulated earlier. One piece of evidence for this is the discovery of α -glycols in reduced peroxide concentrates (13) which are equal in amount to the nonhydroperoxidic peroxides.

As a further illustration of this, during the oxidation of a conjugated triene such as eleostearic acid, the products appear to be mostly hydroperoxides of the same type as those found in the cases of the other fatty acids. The double bond remains intact, although perhaps displaced from its original position (161, 162, 186). There also exist examples of the formation of cyclic peroxides, formed at 37°, in which 1,4-addition of oxygen has been shown to occur (177), as well as 1,2- and 1,6-addition (60), to the conjugated double bond. This could be represented by IV, illustrating the case of 1,4-addition to methyl eleostearate.



Due to the facile formation of hydroperoxides from unsaturated esters, the early investigators were lead to

propose that they were the initial products of autoxidation. However, the lack of a satisfactory source of the energy required for the rupture of an α -methylene carbon-hydrogen bond, which is 80 kcal./mole, had lead various workers in the field to return to the thought that an attack at the double bond was the initial reaction (23, 24, 56, 57, 74). This type of additive attack by oxygen need occur only to a minor degree at the double bonds of a few of the molecules, and then may later continue as a substitutive attack at the allylic position during the predominating reaction. In general, this information suggests a free-radical chain reaction in which a radical is formed, with subsequent rearrangement, and further reaction as is shown by Eq. 6 (57).



One recent proponent of the theory that the initial attack is at the double bond has shown by the use of isotopes, that during the autoxidation of the methyl esters of oleic or 9,10-dideuteriooleic acids the initial attack by oxygen takes place at the double bond during the inherent induction period (97). This is followed by a steady-state period during which the autoxidation propagation is carried out by attack upon the methylenic group in the position adjacent to the double bond.

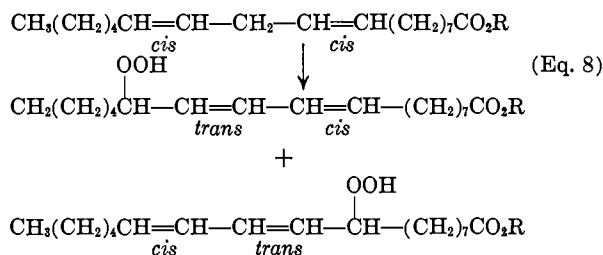
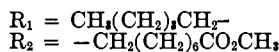
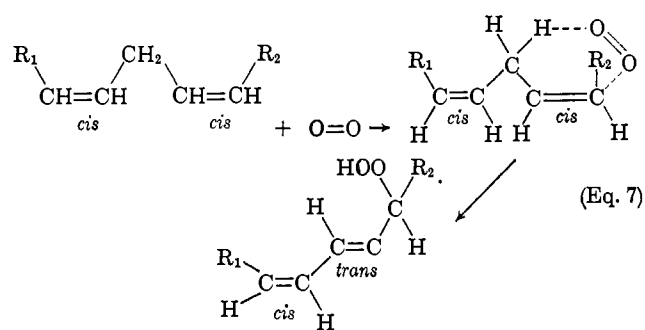
The following mechanism has been postulated, using methyl linoleate, as an illustration of how an activated complex is formed between the π -electrons of a double bond and an oxygen molecule (102). This form is stabilized by hydrogen bonding with the protons of the activated methylene group in the 11-position. The details are shown in Eq. 7.

The diagram has been drawn to illustrate the rearrangement and formation of the 9-hydroperoxy compound, but the same reactions could occur which would result in the formation of the 13-hydroperoxide compound as well. The mechanism explains how the *cis,cis*-olefin is transformed into a *cis,trans* form during the rearrangement, the *trans* bond being the newly formed double bond. Should the reaction consist merely of hydrogen abstraction from the activated methylene group followed by the formation of the peroxide, we

might expect to obtain some equilibrium mixture of *cis,cis* and *cis,trans* forms. It also implies that the 11-hydroperoxy form should not exist.

In actual practice it has been shown that when the amount of oxidation was limited to 10%, only the *cis,trans* isomers of methyl 9- or 13-hydroperoxido-linoleate were formed and no 11-hydroperoxide was formed. These transformations are illustrated in Eq. 8. However, if the material is stored under vacuum, even at temperatures as low as -50° , conversion to the *trans,trans*-conjugated isomer will take place.

As far as the rearrangements of the geometric isomers are concerned, the oxidation of methyl linolenate follows the same pattern as does methyl linoleate during the early stages, since two major conjugated geometric



Other investigations have shown that during the autoxidation of methyl linoleate, 90% of the autoxidation products consists of the two hydroperoxides discussed above (34, 135, 150). It might be expected that the remaining 10% of the products would be the 11-hydroperoxide isomer which has not been isolated to this date. However, in view of the failures of attempts to isolate this material and after the observation that not all of the oxygen absorbed in the oxidation could be accounted for as hydroperoxides (111), the conclusion was drawn that the remainder of the products resulted from the secondary oxidation of the hydroperoxides (137). The proportion of these nonhydroperoxidic substances in the oxygen-containing material increased with increasing temperature. These data tend to verify the hypothesis that some other oxidation products are formed, if only in small amounts, even in the early stages of the autoxidation of nonconjugated fatty acid esters.

Another example that verifies the fact that at the onset of the oxidation almost all of the oxygen is incorporated into fatty acids in the hydroperoxide form is described below. When the initiation of oxidation of methyl oleate was followed at 60, 80, and 100° in a Barcroft-Warburg apparatus, the amount of oxygen taken up was compared to the formation of hydroperoxide during the first 15% of the reaction time (149). It was shown that at 80 and 100°, the relationship could be described by the equation $Y_n = 1.02X^{0.986}$ where Y_n is the amount of hydroperoxide and X is oxygen uptake. Similarly, the relationship between oxygen uptake and total peroxide. Y_c , at three temperatures could be described as $Y_c = 1.09X^{0.986}$. A small, but significant, amount of nonhydroperoxide peroxide seems to have been formed concurrently.

Certain generalizations may be made about the oxidation reactions. It is well known that the rates of oxidative polymerizations vary with the number and degree of conjugation of the unsaturated linkages. However, the actual ratios of reactivity of the different unsaturated acids are evidently not simple relationships and are the subject of some disagreement. For instance, it is reasonable to expect that the number of double bonds of the fatty acid could affect the reactivity, and it has been shown that the rate of oxidation of films of triolein, trilinolein, and trilinolenin was in the order of 1:20:330 (37).

In contrast to the ratio quoted above, other workers believe the relative rates of oxidation of methyl oleate, methyl linoleate, and methyl linolenate to be either in the order of 1:12:25 or to be in 1:2:4 (87). Most of the data for fatty acid esters has been obtained by measurement of the rate of the increase of peroxides or the rates of oxygen uptake. However, some dissatisfaction exists with these techniques since they fail to allow for the decomposition of peroxides during the

course of the reaction. The technique used for the data setting the ratios for the three compounds as 1:2:4 (87) was to measure the constant rate of decrease of the iodine number. This occurs during that portion of the reaction which has been named the maximum rate autoxidation period (MRAP), during which 45-46% of the substrate is destroyed at a constant rate.

To illustrate further the complexity of the situation, when the rates of thermal oxidation of methyl oleate were compared to the rates of oxidation and formation of diene conjugation of methyl linoleate at 20, 40, and 60°, it was shown that the rates for oleate were negligible compared to linoleate (78). However, in the case of photochemical oxidation, the oleate ester was approximately twice as reactive as the linoleate, with the maximum rate occurring at 40°. The ratio of the amount of conjugation to peroxide content of linoleate was also independent of the temperature. A further anomaly is the fact that the oxidation rate of the conjugated 10,12-linoleic acid is only one-third of the nonconjugated 9,12-linoleic acid (2).

The possibility exists that differing mechanisms might operate at various temperatures. In the oxidation of methyl oleate, the attack might be at the allylic hydrogen at 20°, whereas at higher temperatures, there might then be a combination with the double bonds (4, 73). Based on the rate of change in the viscosity of autoxidized linseed oil, some differences are apparent in the course of the reaction in the temperature ranges below 84°, between 84 and 130°, and above 130° (79).

Above 130°, the reaction is distinguished by a negligibly small induction period. Between 84 and 130°, the length of the induction period increases logarithmically as the temperature is lowered, and there exists a point of reaction rate change, after which the rate decreases. No significant difference, however, could be detected at any viscosity in such properties as the refractive index, dielectric constant, or power factor. The reaction has not been studied well at temperatures below 84°, but the induction period extended over a disproportionately longer period of time.

III. PEROXIDE DECOMPOSITION AND CROSS LINKING

Once having been formed, the decomposition of the hydroperoxides with the subsequent cross linking of the unsaturated esters is still complex. Some of the confusion in the literature arises from the fact that a variety of conditions for decomposition have been employed. During the thermal decomposition of fatty acid hydroperoxides, both the scission products and high molecular weight compounds are formed. The scission products are discussed in another section.

Kinetic information about the rate of decomposition of fatty acid hydroperoxides indicates that for a pure sample of methyl linoleate hydroperoxide the rate of decomposition appears to conform to that expected from a first-order reaction. Figure 3 shows that

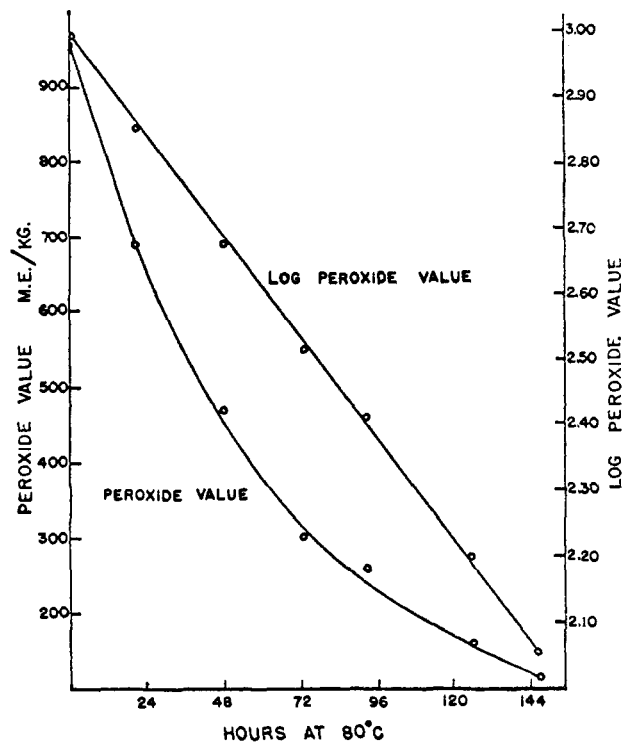


Fig. 3.—The *in vacuo* thermal decomposition of methyl linoleate hydroperoxides (reprinted from ref. 133).

when the material was decomposed at 80°, the plot of the logarithm of peroxide value was a linear function of time (133). However, when the rate of reaction was plotted against peroxide concentration, the reaction appeared to change at higher peroxide concentrations, as shown in Fig. 4. The difference indicates the autocatalytic nature of the peroxide decomposition reaction (133).

The relationship between the increase in temperature during the autoxidation reaction and increase in rate at any given concentration of hydroperoxide does not appear to be simple. It is not unlikely, however, that the kinetics of the reaction can be explained, at least in part, on the basis that the hydroperoxide group functions as a catalyst for the autoxidation reaction (137).

When the peroxide decomposition is carried out at a relatively low temperature, the products appear to be linked through oxygen atoms as evidenced by the following examples. The polymers isolated by molecular distillation from the cobalt oleate catalyzed autoxidation of methyl oleate at 65° appeared to have an excessive amount of oxygen and were resistant to splitting by saponification (163). Also, when methyl oleate

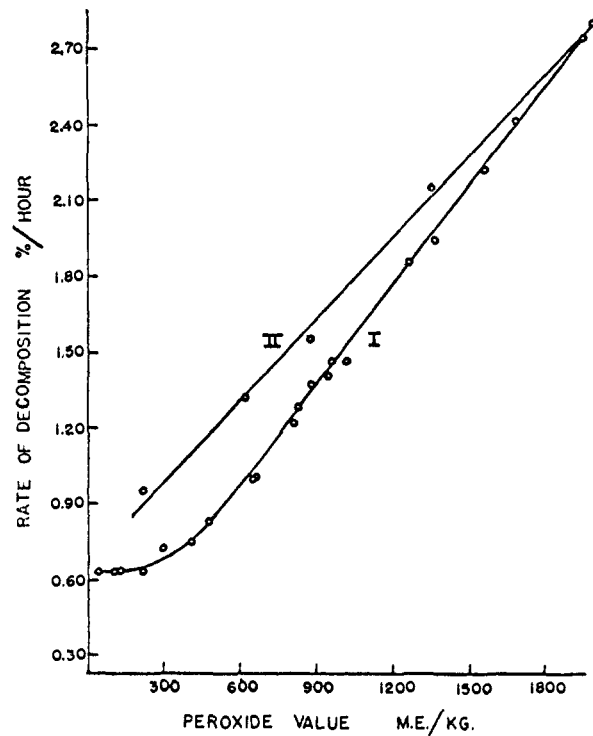


Fig. 4.—The effect of initial peroxide concentration on the rate of the *in vacuo* thermal decomposition of methyl linoleate hydroperoxides: I, autoxidized methyl linoleate; II, autoxidized methyl linoleate diluted with methyl linoleate (reprinted from ref. 133).

hydroperoxide was heated with methyl oleate, mainly oxygen-bonded products were obtained (127). Furthermore, when ethyl linoleate or ethyl linolenate were autoxidized at 30°, the polymers which were isolated by solvent extraction could be split into monomer units by treatment with concentrated halogen acids (36, 191). These various results indicate oxygen-linked units.

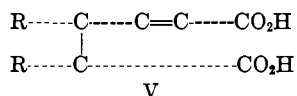
However, when the decomposition was carried out at temperatures exceeding 100° and in an inert atmosphere, the bonding appeared to occur through the carbon-carbon bonded form. When autoxidized methyl linoleate was decomposed at 100° in a nitrogen atmosphere, the dimers which were isolated by solvent fractionation and molecular distillation could not be cleaved by means of hydrogen iodide (190), thus indicating nonoxygen linkages or at least oxygen linkages which are resistant to these reagents.

In more recent studies (62) the autoxidized methyl esters of safflower oil, soybean oil, oleic acid, and linoleic acid were decomposed by heating at 210° for 15 to 30 min. in a stream of nitrogen. The polymer fractions which were isolated in a molecular still were principally dimers, although polymers as large as tetramers were isolated.

The experimental data indicate that the diene reaction did not take part in the polymerization process and no six-membered rings were formed. This was

indicated by the fact that it was impossible to form aromatic structures by bromination with N-bromo-succinimide and subsequent debromination. Usually some unsaturated linkages remained intact. In the case of oleate, this was an isolated *trans* double bond and, in the case of the polyunsaturated compounds, some of the *cis,trans* form of the hydroperoxide had been changed to the *trans,trans*-conjugated form. However, the total amount of diene conjugation decreased in this case. This technique of dimerization seemed to have an effect only upon the hydroperoxides since the addition of alkali-conjugated methyl linoleate did not increase the yield of dimers.

The infrared spectra of the dimers were essentially the same as those of the monomers except for the presence of secondary hydroxyl groups. A small amount of the oxygen present had not been completely accounted for and may possibly have existed in the form of intramolecular peroxides or ethers of difficult reducibility. Except for that possibility, the fact that the dimers were not split by hydrogen iodide indicates the presence of carbon-carbon linkages between chains. The postulated structure, then, based on oxidative degradation, is that of a dibasic ester with unsaturation predominantly on the side of the interchain linkage closer to the carbonyl groups. This should correspond to V (62).



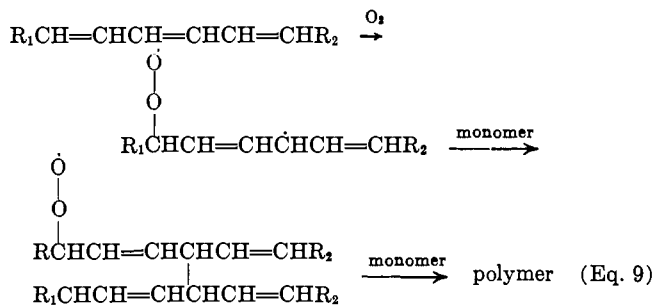
An explanation for the formation of this type of molecule might be that during the thermal degradation of the hydroperoxides through homolytic fission, alkoxy and hydroxyl radicals are formed. These could attack other hydroperoxide molecules to yield water and alkyl radicals that would either combine with themselves or with alkoxy radicals. The substantial loss of conjugation from the unsaturated hydroperoxides suggests that the free radicals might rearrange before dimerization. Also, the radicals, under the conditions used, would be more reactive toward each other than toward the nonradical conjugated or unconjugated esters, and therefore, would tend to form products by dimerization reactions.

In the presence of excess oxygen, considerable difficulty would be expected in forming carbon-carbon linkages instead of carbon-oxygen linkages by the addition of a free radical to an unsaturated position or by the combination of two free radicals. In order to appreciate this more fully, the fact should be kept in mind that the degree of reactivity of oxygen toward free radicals is extremely high. As an example, for an extremely reactive monomer such as styrene, when in equilibrium with air, at least 99.4% of the over-all reaction of styrene free radicals would result in the addi-

tion to oxygen, rather than styrene monomer (114, 116). An unsaturated fatty acid, having internal double bonds would no doubt be even less reactive.

An example involving another conjugated monomer at both moderate and high temperatures involves the oxidation of methyl 9,11-octadecadienoate at 70° (94). A polyperoxide was obtained containing three ester units, no hydroperoxides, 1.8 atoms of oxygen, and one double bond per ester unit. When this material was heated at 210°, presumably decomposing any peroxides, no net change in viscosity or gross composition of the ester could be noted. It was postulated that ether links were formed after the decomposition of the polyperoxide.

In the autoxidation of methyl eleostearate, at temperatures as low as 37°, the polymeric products obtained seemed to be joined mainly by carbon-carbon bonds (60). Dimers and some trimers were also formed. The resulting polymers still contained an average of 1.5 atoms of peroxidic oxygen per fatty acid molecule. This product was reducible by hydrogen iodide, but, since this treatment did not result in the formation of appreciable quantities of monomer, it is believed that the linkages are not simple peroxides. In this case, it is believed that during the formation of the original peroxides by addition to a double bond, the free radical attacks the relatively reactive conjugated ester, containing three conjugated double bonds, to form a low molecular weight vinyl polymer. This is illustrated for the case of 1,4-addition in Eq. 9.



In addition to this, 1,2- or 1,6-addition could also take place. The molecular weight of the polymer would probably not be high, for at each step there would exist the alternative of either cyclization or a reaction with another oxygen molecule and cyclization. The 1,2- and 1,6-addition polymers would retain a conjugated diene system which could react further with oxygen to form mainly cyclic peroxides. In this way a polymeric, but essentially carbon-carbon-linked, peroxide could be built up.

An interesting description can be made here of the well-known, commercial technique of "blowing" of oils. It appears then when linseed oil was blown with air at temperatures ranging between 100 and 200° and samples analyzed at intervals, the following facts

were apparent. The viscosity, saponification number, density, acid number, hydroxyl number, and ethanol tolerance increased with an increase in time and temperature and, in addition, the degree of unsaturation and the drying time decreased. The percentage of peroxide groups rose to a maximum, then declined. The use of cobalt resinate resulted in a higher viscosity, but fewer peroxide groups (189).

IV. CATALYSIS

A. METAL CATALYSTS

A catalyst is a substance which by virtue of its presence affects the rate of a chemical reaction and which may be recovered practically unchanged at the end of the reaction. It is a usually accepted fact that the catalyst is unable to alter the course of the reaction, but merely participates in the formation of a transitory intermediate. It may, however, direct the course of a reaction by favoring the formation of one particular intermediate among several possible species.

It is known that certain metal compounds are useful in increasing the rate at which oils dry, and these drying catalysts can be classified into two groups. One group includes those metals which show a definite accelerating effect on the drying of the unsaturated fatty esters, and the second are those which, when used in combination with driers of the first group, enhance this effect. The first group, the participating driers, include such metals as cobalt, lead, and manganese, which are the most active materials, as well as such other metals as cerium, copper, chromium, iron, tin, vanadium, and zirconium. Certain useful criteria, especially descriptive of the most active metals, are that they exist in two different valences, that the higher valence is less stable, and that they are susceptible to being oxidized from the lower to the higher valence by the hydroperoxides formed during the oxidation of the drying oils (121). These driers aid the drying process by participating in the chemical reactions, and these processes will be discussed below.

The second class of metal-drying catalysts, sometimes called promoter catalysts, include such metals as calcium, zinc, and lead. The exact mechanism of their beneficial action does not seem to be known for certain, but it appears to be of a physical or mechanical nature, such as arranging the disperse phase polymers into a coherent film or by aiding in the improvement of the solubility or mobility of the participating driers (27).

Combinations of compounds of metals from both groups sometimes display enhanced activity and are seemingly able to overcome the adverse effects of water in the drying reaction. For instance, the combinations described in Table I show different reactivities in the presence of water (88).

TABLE I

EFFECT OF HUMIDITY ON METAL CATALYST COMBINATIONS		
Class	Metals	Humidity effect
Fast	Pb-Mn, Pb-Mn-Co, Co-Pb	Little effect above 20°
Intermediate	Co, Co-Mn, Co-Mn-Zn	Large effect at 20-30° Little effect above 40°
Weak	Pb, Pb-Zn, Mn-Zn, Co-Zn	Drying rate depends on humidity

The metallic driers, which are often used industrially in the form of compounds of the naphthenic acids or other aliphatic acids, are believed to catalyze both the formation and decomposition of hydroperoxides. To be truly catalytic, both the oxidized and the reduced forms should perform useful functions, and the oxidation-reduction potential should be such that the reversible reaction is practical under the reaction conditions.

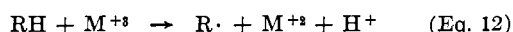
The activity of the metal driers in the oxidation step, *i.e.*, the creation of hydroperoxide, is not completely clear. Several possibilities exist. They may possibly act as oxygen carriers, thereby aiding in the stabilization of the diradical form of the oxygen molecule. This might be accomplished by the association of the oxygen molecule with the unfilled orbitals of the metal, thereby enhancing its activity during the attack at an activated methylene group (10). This would be particularly important at temperatures below 100° (107). This enhanced activity would account for the catalytic effect of the metal. This may be illustrated as in Eq. 10. The alkyl radical may now react with

$$M + \cdot O=O \cdot \rightarrow M-O-O \cdot \xrightarrow{-CH_2CH=CH-} M-O-O-H + \cdot CHCH=CH- \quad (\text{Eq. 10})$$

oxygen and form a hydroperoxide. Besides this effect, there could also be a direct attack of a metal ion upon an olefinic double bond (12) as shown in Eq. 11.

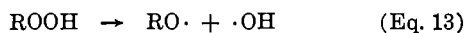


Although this reaction produces a more complicated product, the ion radical might possibly form a hydroperoxide to help initiate the more conventional products of autoxidation. One other reaction that may also be responsible for the direct initiation of oxidation by metallic ions involves a direct attack upon a saturated position as shown in Eq. 12 (10). As verification of

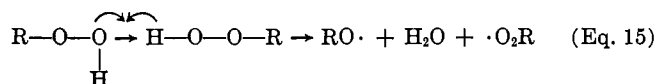


these possibilities, it has been shown by kinetic experiments that there is a difference in the induction period of the oxidation of methyl linoleate when catalyzed by lead, manganese, or cobalt (3). It has also been suggested that the initiation of all autoxidation is due to metal catalysis, since even the most highly purified fatty esters contained traces of metal catalysts (178, 179).

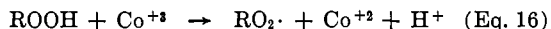
The other type of catalytic activity of metals, the participation in the decomposition of peroxides, can be illustrated by various reactions. For instance, some generally accepted mechanisms for the decomposition of hydroperoxides are shown in Eq. 13 and 14.



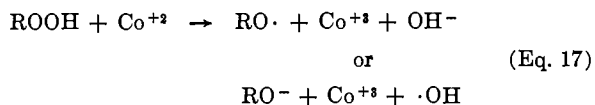
The relative importance of the bimolecular reaction compared to the monomolecular one is known to decrease with increasing temperature and decreasing concentration of hydroperoxides (175). This suggests that a hydroperoxide dimer is responsible (9) as shown in Eq. 15. This reaction may be catalyzed by a



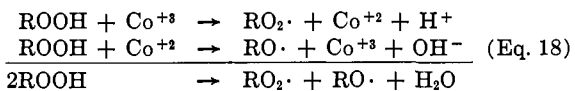
baltic ion in which the rate-determining step is shown in Eq. 16.



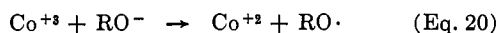
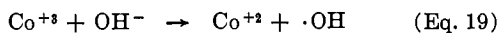
The cobaltic ion is then regenerated by a second, more rapid reaction as in Eq. 17 (10, 11).



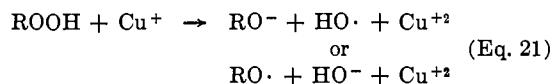
The sum of these two consecutive reactions is seen to be exactly the same as the uncatalyzed bimolecular decomposition reaction proposed in Eq. 14.



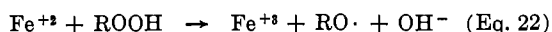
Cobaltic ion is also useful in changing some of the ionic intermediates to the free-radical forms.



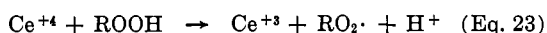
Other examples of the metal-catalyzed decompositions of peroxides include the decomposition of hydroperoxides by cuprous ion (144)



the reductant activity of ferrous ion



and the oxidizing activity of ceric ion.



Cobalt and manganese can act as both oxidants and reductants.

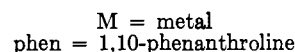
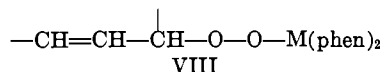
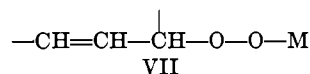
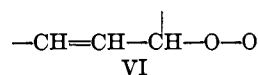
When the catalytic activity of a number of metals was tested at 65 and 120°, it was shown that lead, aluminum, and barium were active in the formation of oleic acid hydroperoxide and thallium and zinc in the decom-

position of the hydroperoxide. Cobalt and vanadium displayed activity in both reactions (154).

An illustration of the fact that the valence state of the metal affects its reactivity is that, whereas metallic copper lowered both the reaction rate and the yield of peroxides in the oxidation of soybean fatty acids (105), cupric stearate was one of the most effective catalysts in the oxidation of linoleic acid out of the list of compounds of cobalt, iron, manganese, cerium, tellurium, and tin (180).

Kinetic data, based on the comparison of the drying times of a coating at different temperatures, have led to some interesting facts on activation energies. For the coatings studied, the energy of activation of the uncatalyzed drying reaction was 17 kcal./mole (187). This same value has also been reported for the autoxidation of pure methyl oleate (95). When 0.005% manganese naphthenate was introduced, the activation energy was reduced to 11 kcal./mole and then further reduced to 7.7 kcal./mole by the incorporation of 1,10-phenanthroline as an accelerator. This information was obtained from plots of the data according to the Arrhenius relationship: $k = Ae^{-E/RT}$.

These data indicate the effect of the addition of a catalyst, in that the reaction path followed by the oil in the presence of the metallic drier requires a lower energy of activation than the path followed in the case in which no catalyst is used. This phenomenon could take place either by lowering the activation energy, E , for a given path or by lowering the energy requirements of a competing path to such an extent that the new reaction course is followed. This might manifest itself in the initiation step where the structures VI, VII, and VIII are postulated.



The data on formation of these intermediates are interpreted to mean that the ease of formation of the intermediates is in the ascending order of compounds VI, VII, and VIII, and that each succeeding one of these is formed with the expenditure of less energy than the previous compound. Besides this effect, termination *via* the joining of two radicals can be minimized by the shielding effect of the metal as in structures VII and VIII. A large concentration of radicals is an undesirable feature because of the possibility of the recombination of two radicals and the termination of the

chain at that point. Consequently, according to this hypothesis, the metal is doubly useful in accelerating the initiation and hindering the termination step of the drying reaction.

The plots of the data in Fig. 5 intersect at an elevated

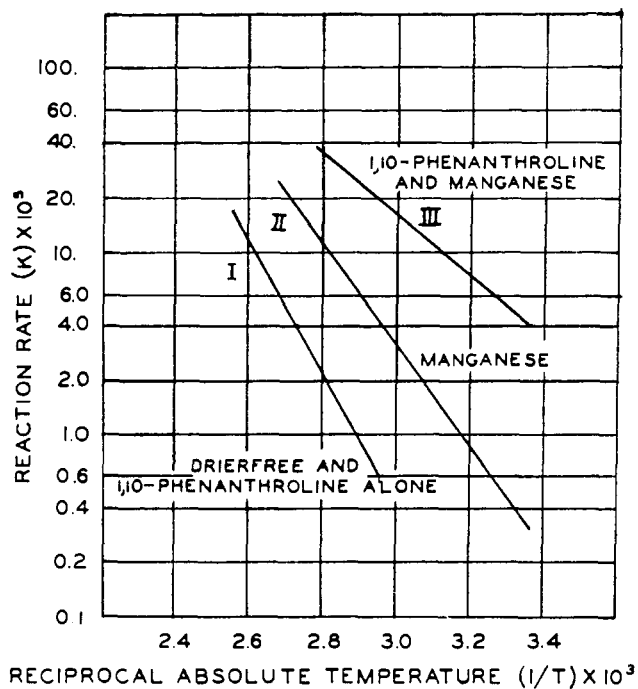


Fig. 5.—Arrhenius plot for linseed oil drying: I, no catalyst; II, manganese naphthenate catalyst; III, manganese naphthenate-1,10-phenanthroline catalyst (reprinted from ref. 187).

temperature, 177° , which is inherent in the fact that the slope of the rate is greater at higher activation energies. This critical temperature and critical rate determine the point beyond which the accelerators and catalysts are useless. This indicates that the over-riding factor at progressively higher temperatures is the fact that a larger population of the drying oil molecules becomes activated sufficiently so as to react without the aid of a catalyst. Thus, the number of molecules which react *via* the intermediate VII, at lower temperatures, exceeds those passing through the intermediate VI, but the situation is reversed at higher temperatures (187).

The advantages of the amine accelerator have been discussed in detail (124, 187). The introduction of a strongly electron-donating ligand splits the energies of the five 3d-orbitals of manganese in such a way that at least one orbital has been made more attractive to oxygen from the energetic standpoint. This type of complexing by means of electron-donating atoms is believed to be possible only from elements of groups V, VI, and VII of the periodic table. The decreasing order of complexing ability of the first row of atoms in the periodic chart is in the descending order of nitrogen, oxygen, and fluorine. However, besides merely the effect of the nitrogen atoms, the resonance

stabilization of an unsaturated molecule enhances its complexing ability. This undoubtedly explains the exceptional activity in this respect of accelerators such as 1,10-phenanthrolines, as well as such complex compounds as hemoglobin, chlorophyll (93), and the metal salts of the porphyrines (54). Care must be shown in the choice of complexing agent, however, as a material such as 1-nitroso-2-naphthol almost destroys the catalytic effect of cobalt (50).

One aspect of the problem that has been neglected so far is the steric factors involved in the attack of oxygen at the unsaturated functional group. The orientation of a free oxygen molecule in its approach to the unsaturated system to form intermediate V may be random, perhaps even including a broadside approach. On the other hand, in the formation of intermediate VI at least a head-on orientation of the metal-oxygen complex is required, with oxygen leading. An attack of the metal end would undoubtedly be fruitless and, therefore, in general, the effective field of attack would be hemispheric, including a solid angle of gyration of somewhat less than 180° . When the metal is further complexed by an accelerator, such as 1,10-phenanthroline, the orientation requirement is much more stringent, with the requirement that the oxygen molecule portion be headed directly at the reaction site for the formation of intermediate VII. The metal and a good portion of the oxygen are shielded by the amine, with the result that reaction zone subtends a much smaller angle. Especially noteworthy is the fact that in spite of these serious stereochemical limitations to the effectiveness of an accelerator, yet, so great is the activation effect, that the net result is the enhancement of the reactivity (187).

B. OTHER CATALYSTS

Besides the use of heavy metal catalysts for the drying of oils, there are still other types of catalysis, involving the use of free-radical or ionic initiators to induce vinyl polymerization of the fatty acids. The free-radical initiators are usually introduced by the addition of an organic peroxide, azo compound, or unstable carbon compound which are capable of decomposition or dissociation. Examples of compounds which will undergo such reactions are hexaphenylethane, hexa-*p*-biphenylethane (89, 90), di-*t*-butyl peroxide (106), benzoyl peroxide (84), *t*-butyl hydroperoxide, and other peroxides (7). Such unsaturated ketones as dibenzilideneacetone and dicinnamoylidene cyclohexanone are also reported to be effective (53).

The use of 0.02% triphenylmethoxy radical or tri-*p*-biphenylmethyl has been reported to reduce the drying time of tung oil from 40 hr. to 5 to 10 min., and the same concentration of diphenylamine radical produced the same results in 2 hr. (90). The reaction catalyzed in this way is believed to involve the formation of a

power for the unsaturated fatty acids containing methylene interrupted multiple bond systems which are in the *cis* configuration.

The considerable reduction of the activation energy of the oxidation of linoleate by lipoxidase, compared to other methods, can be seen from the following listing of activation energies, in kilocalories per mole (21, 23, 169, 170, 173): soybean lipoxidase, 4.3; hematin compounds, 3.3; autocatalysis, 15.2, 17.2; and benzoyl peroxide, 20.5. The rate of linoleate oxidation at 0° for various catalysts were in the order: lipoxidase, 10⁴; hematin compounds, 10²; copper-protein, 1; copper, 10⁻¹; and autoxidation, 10⁻³ (170, 171). The activity of lipoxidase is emphasized by the fact that hematin is considered to be equal in activity to the best of the metal-containing oxidation catalysts.

The mechanism of activity of this catalyst is believed to provide for the specific and definite spacial arrangement of the fatty acid on the surface of the protein (172). The enzyme must absorb oxygen and transfer it to an active site in a definite stereospecific arrangement, thereby creating hydroperoxides with optical activity, as mentioned later in this report (98). As a final part of the scheme, there is also a rearrangement to form a *cis,trans* configuration, presumably due to steric considerations.

The stereochemical requirements of the enzyme are very strict, and only compounds with methylene interrupted unsaturated systems of *cis* configuration are reactive as substrates (14, 138). Examples of reactive acids are *cis*-9,*cis*-12-octadecadienoic acid, *cis*-9,*cis*-12,*cis*-15-octadecatrienoic acid, and *cis*-5,*cis*-8,*cis*-11,*cis*-14-eicosatetraenoic acid. Materials with only one double bond, with conjugated double bonds, or with *trans* configuration are unreactive. Examples of inactive acid are *cis*-9,*trans*-12-octadecadienoic acid and *trans*-9,*trans*-12-octadecadienoic acid. Inhibiting compounds are octanoic acid, *cis*-9-octadecanoic acid, 10,12-octadecadienoic acid, and *trans*-9,*trans*-12,*trans*-15-octadecatrienoic acid.

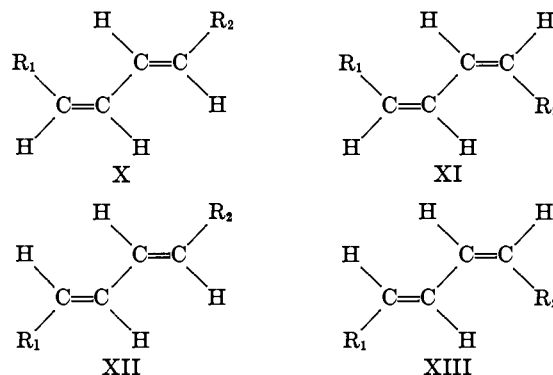
Although the main function of the enzyme appears to be that of an oxidation catalyst, treatment of a substrate with high concentrations of enzyme leads to polymeric materials showing optical activity (138).

V. POSITIONAL AND GEOMETRICAL STEREOISOMERISM

Before the drying process, the unsaturated system of the drying oils is generally in a nonconjugated form and the double bonds are in the *cis* form. Oleic, linoleic, and linolenic acids fit this general description. α -Eleostearic acid, however, has three conjugated double bonds in which the configuration is *cis*, *trans*, and *trans*. During the drying process, the double bonds of the various fatty acids undergo rearrangement to conjugated systems, as well as having the configuration of some of the unsaturated bonds changed from *cis* to

trans. This, in essence, leads to products similar in nature to the structure of tung oil, which is one of the preferred oils for coatings. In order to make use of the acknowledged benefit of the use of the conjugated forms of the unsaturated acids, often attempts are made to isomerize the fatty oils to those structures prior to use.

It can be seen that the number and complexity of positional and geometrical isomers in compounds containing two or three double bonds can lead to numerous possible structures. As an illustration, the four possible arrangements of the conjugated geometrical isomers of a diene are shown below as structures X–XIII.



The configuration of the double bonds are: X, *cis,trans*; XI, *cis,cis*; XII, *trans,trans*; XIII, *trans,cis*.

The possible configuration for a triene is even more complicated—the existence of eight geometrical isomers being possible. They are

- | | |
|-------------------------|-----------------------------|
| 1. <i>cis,cis,cis</i> | 5. <i>cis,trans,trans</i> |
| 2. <i>cis,cis,trans</i> | 6. <i>trans,trans,trans</i> |
| 3. <i>cis,trans,cis</i> | 7. <i>trans,trans,cis</i> |
| 4. <i>trans,cis,cis</i> | 8. <i>trans,cis,trans</i> |

In both cases, there also exists a number of possible types of positional isomers, three in the case of the diene and five in the case of the triene (43). Thus, it may be seen that the numerous structures possible due to rearrangements such as illustrated in this section present a complicated situation. The benefits of the alteration in structure are not simple to evaluate in view of the balance due to the improvements in reactivity caused by conjugation *vs.* the reduction in reactivity due to *trans* bond formation. One example of the difference in reactivity of the different *cis,trans* isomers is that oleic acid (*cis* bond) can be more easily oxidized than elaidic acid (*trans* bond) (32).

The ability of oxygen molecules to exhibit hydrogen bonding accompanied by the formation of a six-membered ring with subsequent rearrangement of the unsaturated linkage to form a hydroperoxide has been discussed in a previous section. It has also been pointed out that this process is accompanied by the conversion of a *cis* bond to the *trans*, less reactive, form. Other isomerization agents can cause this same *cis,trans* interconversion, and examples of these include such

compounds as sulfurous acid or a saturated solution of sodium bisulfate, phosphorous acid, sulfur, selenium, nitrous acid, iodine, and nitrogen dioxide. Their action is believed to stem from some form of complex formation (100).

The *cis,trans* interconversion of oleic acid, as well as the methyl esters of oleic, linoleic, and linolenic acids, has been studied, in which the catalysis was provided by means of oxygen or nitrogen dioxide (100). The behavior of nitrogen dioxide is believed to occur through the formation of a series of complexes with the π -electrons of the double bond during the isomerization reactions. In general, it is believed that the initial reaction might lead to a molecular complex which then passes through a transition state involving a labile *trans* configuration and a transient existence of a carbon-carbon single bond. This polarized bond is now free to rotate and the subsequent recovery of the π -electron by this carbon-carbon bond may then release the nitrogen dioxide molecule and form the more stable *trans* double bond as well as a lesser amount of *cis* double bond.

It is interesting to note that ultraviolet light, by imparting energy to a system, is instrumental in converting *trans* isomers to *cis* isomers. This is contrary to the action of most isomerization agents.

The effective use of alkaline materials for the purpose of catalyzing the shift of a double bond dates back to 1840 when fused potassium hydroxide was used successfully to isomerize oleic acid, so that the double bond evidently became conjugated with the carbonyl group (184). Later work clarified this isomerization ability of various types of compounds.

These isomerizations can be catalyzed in various ways. For instance, alkali can cause linoleic acid to isomerize to the point at which 90–95% of the acid is conjugated (125). Treatment with iodine then caused the isomerization of 60% of the material from the *cis,trans* unsaturated form to the *trans,trans* form. Among the alkalis useful in effecting conjugation are potassium hydroxide (171), potassium *t*-butoxide (188), and sodium amide in liquid ammonia (1).

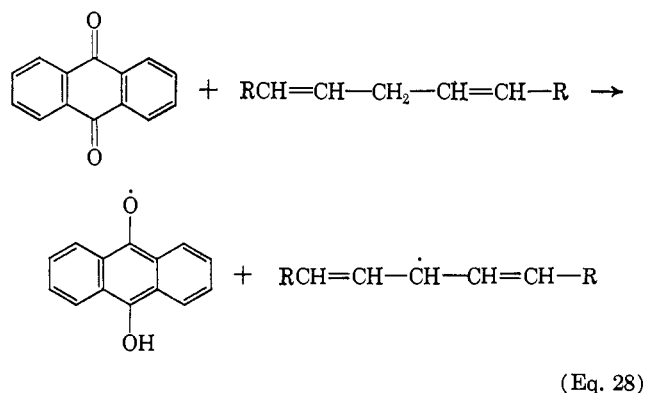
An explanation of the mechanism of the shift of the double bond in the presence of alkali makes use of an ionic intermediate involving the abstraction of a proton. This is described schematically in Eq. 27. As for the

$$\begin{array}{c} R_1CH=CH-CH_2-CH=CH R_2 + OH^- \rightarrow \\ R_1CH=CH-CH-CH=CH R_2 + H_2O \\ \uparrow \\ R_1CH=CH-CH=CH-CH-R_2 \text{ (Eq. 27)} \\ R_1CH=CH-CH=CH-CH_2R_2 \xleftarrow{H^+} \end{array}$$

useful nickel-carbon catalyst, it is believed that the material, being a strong hydrogen acceptor, will complex with a hydrogen atom and provide the same type of intermediate as shown above, although the explanation has been presented that it takes place by means

of a free-radical mechanism (43). When methyl linoleate was heated on a palladium-carbon catalyst at 200°, the maximum amount of conjugation, 24%, was attained in 4 hr. (168).

Quinoid compounds are also effective. Among various quinones tested, 2-chloroanthraquinone was the best, producing 17.2% diene conjugation in soybean oil after the reactants were heated together for 2 hr. at 280°. Quinone, itself, catalyzed the formation of only 3.6% conjugated material (140). A mechanism explaining the usefulness of quinones in catalyzing the formation of conjugated compounds is illustrated in Eq. 28 for anthraquinone (146). As has been explained

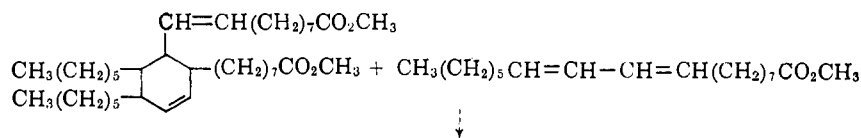


previously, this structure could then rearrange to produce a conjugated system, although dimerization is also caused by the same catalyst. Both reactions, *i.e.*, conjugation and dimerization, increased in rate with increasing concentrations of catalyst, but after the limiting concentration, 0.5%, only the rate of conjugation increased. Various iodides such as the salts of sodium, potassium, lithium, cadmium, and mercury are useful in changing α -eleostearates to β -eleostearates in tung oil (129). Examples of other materials useful for producing conjugation are sulfur dioxide and furfural (143).

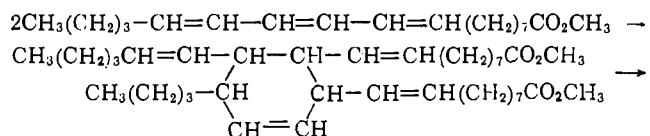
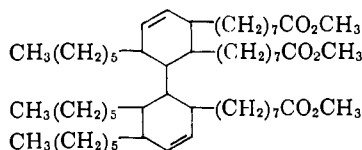
It was previously pointed out that the beneficial effect of the incorporation of conjugated double bonds instead of the more common isolated double bonds is unfortunately tempered by the reduced reactivity of compounds containing *trans* linkage compared to *cis* linkage. The compromise in reactivity brought about by combinations of these systems is shown in Table II where the reactivity of various compounds is exemplified by oxygen absorption (123). This table shows how

TABLE II
OXIDATION OF OCTADECATRIENOIC ACIDS AT 40°

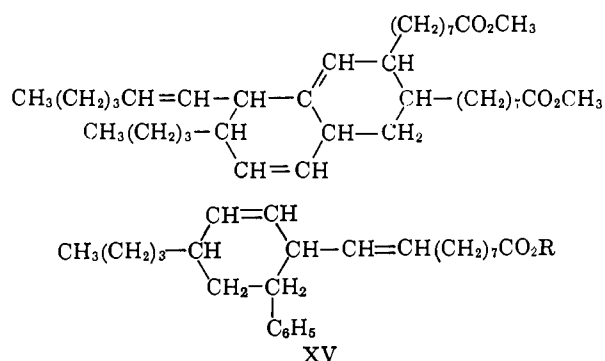
Compound	Mole O ₂ /mole acid/100 min.	Unsaturated bond configuration
α -Eleostearic acid	2.68	<i>cis,trans,trans</i> conjugated
β -Eleostearic acid	1.02	<i>trans,trans,trans</i> conjugated
Linolenic acid	0.52	<i>cis,cis,cis</i> unconjugated



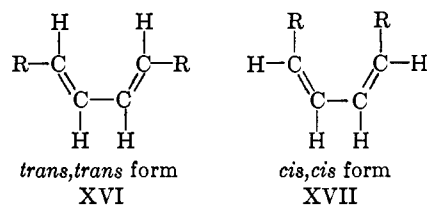
(Eq. 30)



(Eq. 31)



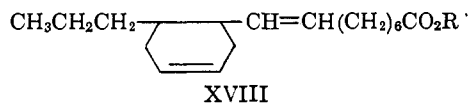
The most desirable configuration about the unsaturated linkages during the diene reaction is the *trans,trans* conjugated configuration. The *cis,trans* form is less suitable and the *cis,cis* form is unsuitable. These facts can be deduced from the inspection of Fisher-Hirschfelder-Taylor models of such molecules, which made it apparent that in the first case there is no interference to rotation around the central bond, whereas in the last case there is considerable steric hindrance (131). Therefore, the *cis,cis* form could not easily form the stretched or boat form necessary for ring formation whereas the *trans,trans* form could form these shapes. These forms are shown as structures XVI and XVII. As a further illustration, it is



well known that *trans*-piperylene will undergo the diene reaction with maleic anhydride, whereas the *cis* isomer does not yield a cyclic product (46). In the case of fatty acids, it has been shown that when Diels-Alder adducts were made from maleic anhydride with *trans,trans*-9,11- and *trans,trans*-10,12-linoleate, the reactants

combined completely, whereas alkali-isomerized linoleic acid, presumably the *cis,trans* form, reacted only slightly (181). Directly in keeping with this information are the relative rates of polymerization at 290° to a 60% yield. For *trans*-10,12-linoleate, alkali-conjugated linoleate, and nonconjugated linoleate the rates are in the ratio of 40:7:1 (131). These materials evidently have the structure: *trans,trans*; *cis,trans*; and *cis,cis*.

Besides this sort of bimolecular reaction, it has also been established that monomolecular cyclic structures are formed during this same process, with the structures similar to XVIII (113).



Various isomers of this same general structure, 1-propyl-2-alkenecarboxycyclohexene, have been formed which differ only in the position of the double bond in the side chain. A monocyclic compound containing only one double bond has also been obtained from the heat treatment of methyl linoleate (118).

In conclusion, this technique appears to involve both intramolecular and intermolecular reactions between the glyceride molecules, with the latter playing the major role. Ring closure probably occurs between fatty acid groups of two different glycerides, and this accounts for the increase in viscosity of the oils. Condensation between fatty acid groups in the same glyceride molecule may also occur (19).

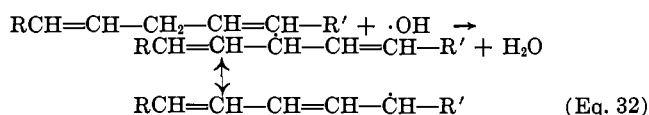
The effect of pressure in thermal polymerization was illustrated when linseed oil was polymerized at 310° at pressures varying from atmospheric to as low as below 1 mm. (108). At the lowest pressure the oils had a higher density, higher molecular weight, and lower acid number, were freer of volatile matter, and were more viscous than those subjected to higher pressures. There appeared to be no difference in the oils obtained at pressures between 100 and 760 mm.

In this type of polymerization, the course could be affected by the reaction time, temperature, and the amount of water used as a catalyst. Of various conditions tried, the best yield of linoleic acid dimer was obtained when the acid was heated at 390° for 5-7 hr. with 5% water used as a catalyst (160).

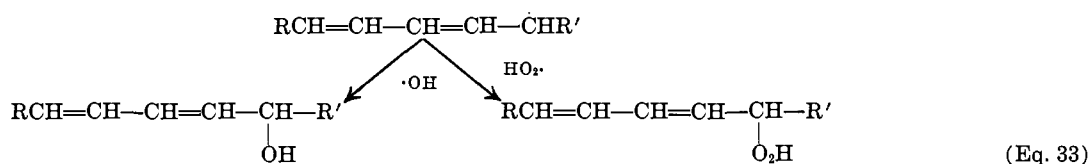
VII. HIGH ENERGY IRRADIATION

The exposure of drying oils to high energy irradiation has been examined to some extent. This examination could be conducted under different sets of conditions, either in aqueous solution or in pure form, and in the absence or presence of oxygen. The action of ionizing radiation upon air-free water is believed to give rise mainly to hydrogen free radicals and hydroxyl free radicals which are capable of combination to produce hydrogen and hydrogen peroxide molecules. In the presence of oxygen, the $\text{HO}_2\cdot$ radical can also be produced.

When aqueous solutions of drying oils are irradiated in the presence of air, the reactions proposed for the autoxidation are shown in Eq. 32 (117).



This radical now can be oxidized further to form the hydroperoxides normally expected in the autoxidation reaction and to start the chain reaction. Termination reactions can be formed by a high dose rate due to the production of a large number of $\cdot\text{OH}$ and $\text{HO}_2\cdot$ particles. This is illustrated in Eq. 33.



When pure liquids are irradiated in the absence of water, the free radicals formed are evidently due to the ejection of an electron, accompanied by the loss of a proton, to form a radical. The radicals could either polymerize or form peroxides, depending on the presence or absence of oxygen.

Various radiation techniques which appear to be useful in aiding the drying of oils are electrical discharges, Van de Graaff generators, γ -rays from sources as Co^{60} (38, 75) and X-rays (117). A nonelectronic form of high energy, that is, the use of supersonic energy, also has helped to accelerate the autoxidation of sardine oil (148).

When mineral oils or fatty oils are subjected to the action of a glow discharge at low pressures and moderate temperatures in a hydrogen or nitrogen atmosphere, a considerable increase in viscosity is effected presumably because of polymerization of the starting material. This is sometimes known as the "Electrion" or "Volto" process. The properties of the drying oils treated by this process, such as the hardness and resistance of the film after drying, have been described as being better than those of thermally polymerized oils (70).

When linseed oil was submitted to an electrical discharge, in a hydrogen atmosphere at low pressure and at 70° , the molecular weight of the oil increased approximately 65% in 17.8 hr. (18). It was assumed that some hydrogenation of double bonds had taken place, but there was no destruction of carboxyl groups. It was believed that the changes that occurred were due to intermolecular bonding through the combination of free radicals which had been formed previously by the action of hydrogen atoms (16, 183). The polymeric materials formed were composed equally of dimeric and trimeric forms and were low in cyclic structure content. This contrasts with the materials formed by thermal polymerization, which have a high content of six-membered rings formed through the diene reaction. One interesting difference in the products of the two processes is that when 60% of the glycerides of linseed oil were polymerized by either technique, the material made by the thermal process had a viscosity over nine times greater.

Besides linseed oil, other oils such as soybean, cuttlefish, and other fish oils displayed improvements in dryability when exposed to a silent electric discharge under atmospheres such as hydrogen, nitrogen, or carbon dioxide (69, 72). A discharge of 500 cycles and 11

kv. polymerized castor oil under a hydrogen atmosphere (71).

High energy radiation has also been used successfully in causing the oxidation of drying oils. When methyl oleate was irradiated with γ -rays at 56 and 75° , hydroperoxides were formed (157), which were mixtures of four different isomers with substitution existing on the following positions in the descending order of 10, 11, 9, 8. It can be seen that this is not a significant departure from nonirradiation-induced autoxidation. When drying oils were exposed to high energy radiation, the reactions which occur, in general, were similar to those which took place during autoxidation. Although it had previously been shown that during the initial stages of autoxidation conjugated dienes accumulate in direct proportion to hydroperoxide group formation, and that the proportion is virtually the same at all temperatures between 20 and 80° (11), a higher proportion of conjugated diene was formed in methyl linoleate when exposed to irradiation than in normal autoxidation (38). It is believed that this may be because in the presence of a large concentration of free radicals and with only a limited supply of oxygen, a high proportion of non-

hydroperoxide products would be formed.

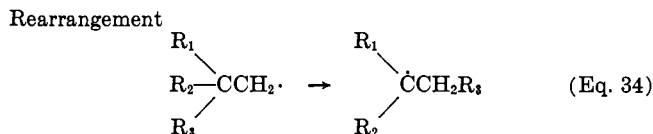
One of the effects of irradiating oil is that of bleaching (109). This may be carried out by means of γ -rays from Co^{60} , a linear accelerator, or a Van de Graaff generator. The bleaching action varies logarithmically with the size of the dose and is inhibited by oxygen, and is believed to be caused by the saturation of materials containing conjugated double bonds. Some of the hydrogen necessary for this action could be obtained from the decarboxylation of fatty acids and from the irradiation of the solvents. Another interesting aspect of this technique is the fact that when the same material was irradiated in the solid crystalline form at low temperature, insoluble polymers were formed, a phenomenon not observed at higher temperatures. This is probably due to the creation of a number of conjugated diene free radicals in close proximity, which had an opportunity to combine to form polymers when the crystal collapsed during the liquefaction of the sample.

During this process, the reactions are accompanied by the formation of undesirable flavors which are especially significant in foods. The flavors can be formed whether the irradiation is performed in the presence or absence of oxygen. Although there is a correlation between peroxide values and flavor strength in autoxidized fatty acid esters, no good relationship exists in the case of irradiated esters. More marked flavor changes occur in the presence of oxygen but definite changes also occur when special precautions had been taken to eliminate all free oxygen. This, of course, does not necessarily mean that the major flavor components are devoid of oxygen. There still exist sources available in the carboxyl group of the esters, as well as adsorbed gases on the glass walls of the containers. The best explanation for the cause of the poor flavor is the presence of carbonyl-containing compounds. The formation of the various types of carbonyl compounds is discussed in a later portion of this report.

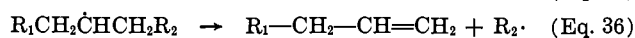
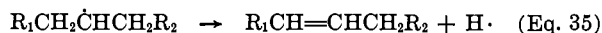
One other aspect of the use of electrical energy is the anodic polymerization of tung, linseed, or castor oils at 40–50° (132). This process does not become exothermic and the conductive salts needed for the anolyte are selected from such useful drying metals as cobalt, manganese, and lead.

VIII. DECOMPOSITION PRODUCTS

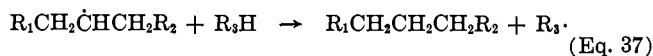
It is inherent in a process in which oxidative attacks upon a hydrocarbon skeleton take place with the formation of free radicals, such as in oxidative polymerization, that the concept of decomposition should arise. The oxidation itself is a form of decomposition while the involvement of free radicals permits certain side reactions to occur. Reactions typical of free radicals are listed in Eq. 34–37.



Scission



Abstraction of hydrogen



In all of these reactions the concept of decomposition or alteration of the original structure is present except in Eq. 37. In this case the active species is merely transferred to a different molecule which is then faced with the same possibilities as shown above.

Along with the products which are known to form the main reactive species in the oxidative polymerization of fatty acids and which have been discussed in previous sections, there are numerous references to "other oxidation products." These other oxidation products are produced even during the low-temperature oxidation of drying oils and are more or less disagreeable depending on whether the materials in question are part of, or come into contact with, foods. One common oxidation product is water, along with various low molecular weight organic compounds.

It has been shown by the use of isotopes of hydrogen that the formation of water during the autoxidation of methyl oleate results from the primary decomposition of hydroperoxides, and the formation of organic volatile products results from secondary decomposition, at a later stage (97). During oxidation at 75° the first stage lasts for 125 hr. and only after 150 hr. are volatile organic compound products formed (99).

Various contributors to this field have studied the volatile decomposition products produced by the oxidation of materials containing oleic, linoleic, and linolenic acids, as well as saturated acids. By various techniques such as solvent fractionation and chromatography as well as the preparation of derivatives, some of the organic decomposition products have been isolated and identified. They include such compounds as listed in Table III.

The presence of the semialdehyde esters such as azelaaldehyde (64, 126) and hydroxyalkyl peroxide containing chains of seven or eight carbon atoms (65) have also been shown.

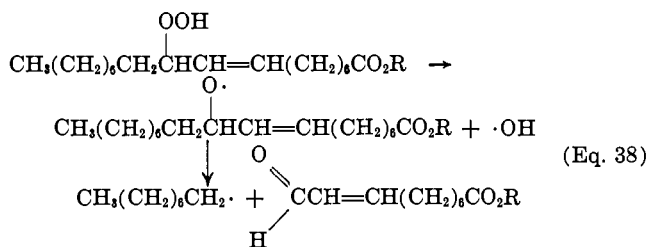
The mechanism of the formation of all of these various decomposition products, along with the others that undoubtedly exist but have not been enumerated here, has not been formulated completely. However, the structures of intermediates leading to some of the known products will be suggested.

An explanation for the formation of aldehydes by the decomposition of an oleic ester is illustrated in Eq. 38

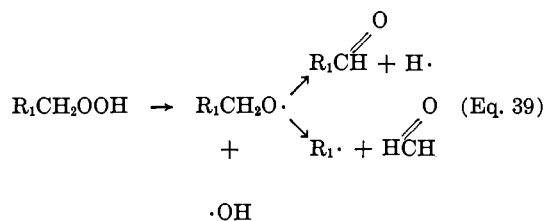
TABLE III
 DECOMPOSITION PRODUCTS OF FATTY ACIDS

Carboxylic acids ^a	Ketones ^b	Aldehydes ^c	Volatile gases ^d
Formic acid	Methyl ethyl ketone	Acetaldehyde	Carbon monoxide
Acetic acid	Methyl vinyl ketone	Propionaldehyde	Carbon dioxide
Valeric acid	Methyl <i>n</i> -amyl ketone	Acrolein	Hydrogen
Caproic acid	Methyl <i>n</i> -hexyl ketone	Crotonaldehyde	
Heptanoic acid	Methyl <i>n</i> -heptyl ketone	Pentanal	
Caprylic acid	Methyl <i>n</i> -octyl ketone	2-Pentenal	
Pimelic acid	Di- <i>n</i> -butyl ketone	Hexanal	
Suberic acid	Diamyl ketone	3-Hexenedial	
Pelargonic acid	Dinonyl ketone	Heptenal	
Azelaic acid		2-Octenal	
Capric acid		Nonanal	
Sebacic acid		2-Nonenal	
Undecanoic acid		2,4-Decadienal	
		2-Undecenal	

^a Ref. 48, 65, 85, 91, 104, 153. ^b Ref. 48, 85, 92. ^c Ref. 5, 35, 48, 85, 92, 165, 167. ^d Ref. 141.

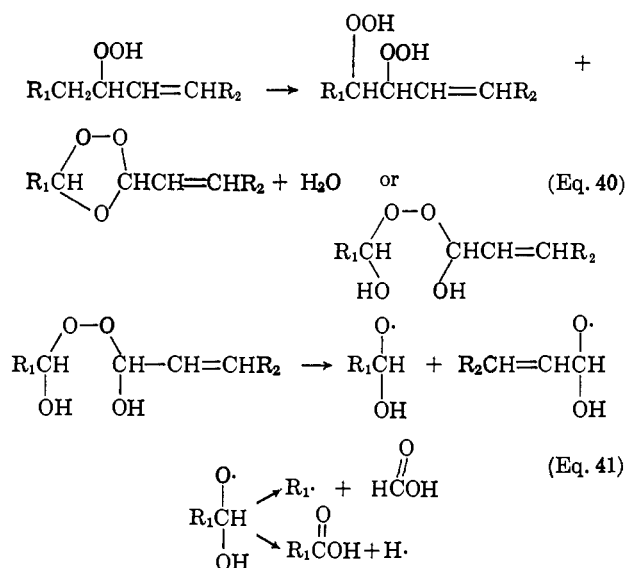


(65). Such free radicals can interact with more oxygen, form hydroperoxides by the chain propagation mechanism, and eventually produce lower aldehydes by the same process as shown in Eq. 39. The oxidation of

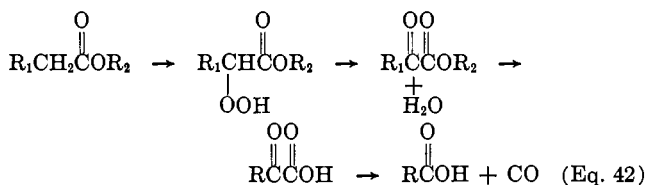


some of the aldehydes might account for the formation of the mono- and dibasic acids reported, some of which may be unsaturated.

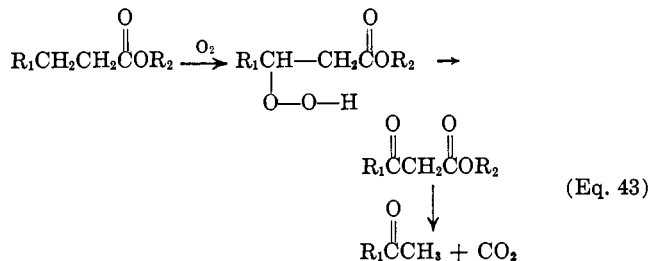
Another pathway for the formation of carboxylic acids has been postulated by the decomposition of ozonides. This might result in the formation of formic and higher molecular weight acids as shown in Eq. 40 and 41 (65, 142).



Although the preferred oxidative reactions are in the vicinity of the unsaturated linkage in the fatty acid, sometimes, especially in the case of saturated compounds, an attack can take place at the α -carbon of the acid radical followed by the formation of keto acids, with subsequent decomposition as in Eq. 42 (48).

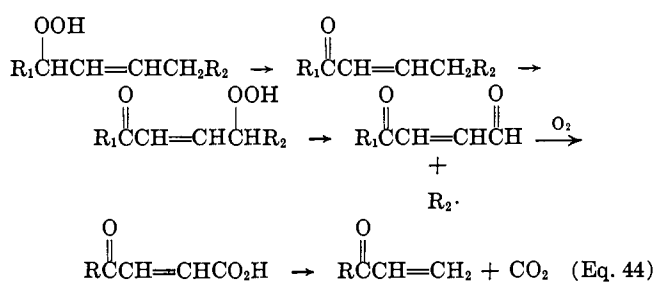


These stepwise α -oxidative reactions could account for the presence of the numerous carboxylic acids found, as well as carbon monoxide, in the decomposition products. This form of attack is probably more effective with free fatty acids than with glycerides. The consequence of oxidative attack at the β -carbon atom of the acid radicals can be seen in Eq. 43 in the formation of methyl ketones, as well as carbon dioxide.



Vinyl ketones can also be formed by oxidation in the neighborhood of the double bond as shown in Eq. 44 (48). These vinyl ketones might decompose further to form methyl ketones.

In the complete absence of atmospheric oxygen, triglycerides can be cracked, and in the temperature range of 245–260° products such as acrolein, ketones, and carboxylic acids are formed (48).



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