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Autoxidation¹

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FEW other reactions of fatty materials have been the subject of such intensive study as their reactions with molecular oxygen. In spite of this, relatively little is known about the structures of many of the products of autoxidation, and about the mechanisms by which they are formed. Much progress has been made in recent years in elucidating the nature and the mechanism of formation of certain initial products, namely the peroxides; on the other hand, little is known about the reactions involved in the development of a host of secondary products that are formed from the peroxides, or formed concurrently with them.



W. O. Lundberg

Because of the tremendous number of papers that have been published on the subject of autoxidation, most of the people who have contributed to

the information that is summarized in this presentation will not be named, nor will a bibliography be given. Instead the interested student is referred to two recent general reviews of autoxidation for selected bibliographies.²

¹ Hormel Institute publication no. 111.

² S. G. Morris, *Agricultural and Food Chemistry*, **2**, 126 (1954); R. T. Holman, "Progress in the Chemistry of Fats and Other Lipids" by Holman, Lundberg, and Malkin, vol. 2, p. 51, Pergamon Press Ltd., London (1954).

Importance

Perhaps major impetus to researches on the autoxidation of fats and oils has stemmed from the problem of rancidity in edible fats and oils. Autoxidation is responsible for a most important type of rancidity, common oxidative rancidity, that occurs typically in edible fats such as lard and vegetable shortenings. Rancidity is not a major problem in relation to the uses of inedible glycerides; nevertheless the odor of rancid fat is sufficiently offensive to be undesirable even for some actual or potential uses of inedible fats.

In relation to non-food uses of fats and oils, autoxidation assumes major importance in the drying of protective coatings and printing inks prepared from triglyceride oils. The oxidation reactions are a prerequisite to the polymerization reactions that lead to the formation of hard, durable films. As will be pointed out later, autoxidation plays not one role, but several, in the formation of solid films.

Not enough information has been available about the autoxidation of fats and oils to permit any type of control or selection in the multiplicity of reactions and products, and hence no appreciable development of industrial products through autoxidation of inedible glycerides has occurred. Knowledge about the nature of the autoxidation reactions is growing more rapidly than ever before however, and in addition, techniques are becoming available for the separation of various products of autoxidation. The future for the development of new products from inedible glycerides on the basis of autoxidation reactions therefore appears promising.

The main purpose of this discussion is to summarize chemical and physico-chemical aspects of the autoxi-

dation of fats. The importance and possible applications of the reactions will receive a slight amount of additional attention in later stages of this paper.

Historical

More than 125 years ago it was recognized by the French chemist, DeSaussure, and the Swedish chemist, Berzelius, that triglyceride oils undergo chemical reactions with oxygen of the air. The former observed a pronounced induction period in the oxidation of walnut oil, followed by a period of rapid absorption of oxygen accompanied by the production of carbon dioxide. The latter observed that linseed oil distributed on wool oxidized so rapidly that the heat generated caused the oil to ignite.

The next 100 years saw only a very slow development of knowledge about the autoxidation of fats and oils. It was established that the initial products consisted largely of peroxides and that among the secondary products were various aldehydes, ketones, and acids which were in large measure responsible for rancid flavors and odors. For many years it was believed that oxygen combined with unsaturated oils by direct addition at the double bonds, and that cyclic peroxides were formed even though convincing chemical evidence for such structures was never obtained.

It has since been established that most of the peroxides formed with unconjugated unsaturated fatty acid esters do not have cyclic structures. It has generally been accepted that cyclic peroxides are formed predominantly in the oxidation of esters of conjugated fatty acids. However, and more recently, indirect evidence of the possible formation of appreciable amounts of cyclic peroxides in the autoxidation of oleates has been obtained.

A number of years before any real knowledge of the structures of the peroxides had been achieved, Alyea and Bäckstrom gave a remarkably accurate description for their time of the mechanism of autoxidation in fats. They postulated a chain mechanism, largely on the basis of the observation that the reactions could be markedly inhibited by very low concentrations of various organic substances. To be sure, the nature of the "activated" molecules involved in their chain mechanism was not clearly understood by them. It was thought that the activation involved some kind of thermal excitation whereas now it is known that the activated molecules are in reality free radicals.

For many years, in the field of petroleum chemistry, attention has been given to the autoxidation of olefinic materials, and an appreciable amount of information concerning the nature of the products and the mechanisms of the reactions has been obtained. Much of this information has been of value in shedding light on the autoxidation of fatty materials, but for some obscure reason research workers in the field of fat and oil chemistry have frequently ignored, until recently, the findings of workers in petroleum chemistry which could have speeded progress toward a better understanding of autoxidation in fats.

Modern Advances

About 15 years ago Criegee reported that cyclohexene could be autoxidized to yield a peroxide without any appreciable decrease in the original unsaturation. Farmer and his coworkers confirmed this observation and found that it held also for the autoxidation of

unsaturated fatty acid esters. Other evidences indicated that the peroxides were in reality hydroperoxides and that the hydroperoxide groups were attached to a carbon in an alpha position relative to a double bond. A further important conclusion was that free radicals were involved in the formation of the hydroperoxides. These observations and conclusions opened the door to rapid progress in the accumulation of new information about the nature of the autoxidation of fats, and rapid progress continues to this day.

In this short course one of the objectives is to consider the chemical reactions of inedible glycerides. The fact is however that most of the important fundamental information concerning the autoxidation reactions of fats has been obtained on simple esters of monohydric alcohols and individual fatty acids. Much of the discussion in this paper will therefore be concerned with such esters. This approach is justified because the same information is almost equally representative of what takes place in the autoxidation of triglyceride fats and oils.

Autoxidation of Linoleates

Studies of the autoxidation of esters of common polyunsaturated fatty acids have revealed that, concomitantly with the formation of peroxides, double bond shifts occur in such a way that considerable proportions of conjugated systems are formed. This discovery was made by means of ultraviolet spectrophotometry. In the case of linoleates it was found that, as a result of autoxidation, a strong absorption band appeared in the wavelength region of 232 m μ . It is in this region that conjugated dienes show strong absorption.

It was therefore postulated that, in the autoxidation of linoleate, a hydrogen radical was removed from the 11 carbon atom, leaving a resonance hybrid that could be stabilized by the addition of an oxygen molecule and atomic hydrogen at any one of three positions. Attachment of the resulting hydroperoxide group at the 9 or 13 position would yield conjugated diene hydroperoxides; attachment at the 11 position would lead to a nonconjugated product.

Various research workers observed that the ultraviolet spectral absorption of autoxidized linoleate was appreciably lower than was to be expected on the basis of available information if the conjugated diene groups and peroxide groups were formed in a 1 to 1 molar ratio. From the then available extinction coefficients for pure conjugated diene systems, it was calculated that the hydroperoxides formed in the autoxidation of linoleate under ordinary conditions were approximately 70 to 85% conjugated. By inference, the balance was 11 hydroperoxide that contained no conjugated unsaturation.

On the other hand, when autoxidized linoleate was hydrogenated and the resulting products were separated chromatographically on alumina, it was possible to isolate only the 9 and 13 monohydroxystearates. No 11 monohydroxy stearate was found. Because of the somewhat indirect nature of this evidence however it was not considered to preclude the possibility that an appreciable amount of 11 monohydroperoxide was formed.

The belief that some unconjugated hydroperoxide is formed in the autoxidation of linoleate was given impetus by the results of studies of the lipoxidase-catalyzed oxidation of linoleates. In this case a con-

siderably higher molecular extinction coefficient at 232 $m\mu$ was observed than in the case of autoxidized linoleate, and indeed the observed molecular coefficient agreed closely with the anticipated value for peroxide with 100% conjugation.

Subsequent studies have revealed that the somewhat lower spectral absorption in the case of autoxidized linoleate is not due to the presence of unconjugated peroxides. It has been found that the lower absorption can be accounted for on the basis of the geometric configuration of the double bonds. Infrared spectrophotometry has shown that appreciable quantities of *cis,trans*, and *trans,trans* conjugated diene systems are formed and that the differences in the ultraviolet spectral absorption for different geometric forms are responsible for the somewhat lower than anticipated values for autoxidized linoleate. In studies in which hydroperoxides of linoleate have been isolated in concentrated form and analyzed, the products have been found to contain at least 90% conjugated diene, and more probably the figure is very near 100%.

The formation of *cis,trans* conjugated diene hydroperoxides is to be expected by analogy with other reactions involving double bond shifts. It has been found in the alkali isomerization of unsaturated fatty acids that a *cis* double bond that changes position assumes the thermodynamically more stable *trans* configuration. In autoxidized linoleate however large proportions of *trans,trans* conjugated diene may be found, as shown by infrared spectral data. The inversion of the double bond that has not been shifted in the autoxidation reaction appears to take place, not during hydroperoxide formation, but in a subsequent reaction. When the conjugated *cis,trans* system has once formed, an inversion of the second *cis* double bond might be expected to take place by analogy with the conversion of alpha eleostearic to beta eleostearic acid. The latter reaction takes place easily in the presence of sulfur and light. With autoxidized linoleate it is possible that the conversion to a *trans,trans* form is catalyzed by the peroxides themselves.

Mechanism of Peroxide Formation

The mechanisms involved in peroxide formation in the autoxidation of fatty acid esters have been established primarily by researches conducted in the laboratories of the British Rubber Producers' Association. In studies of the oxidation of ethyl linoleate at 37°C. it was found that the rate of oxidation was related to several factors.

First, the rate of oxidation was found to be directly proportional to linoleate concentration. Second, the rate of oxidation was found to be a straight line function of the extent of oxidation. Since virtually all of the oxygen went initially into the formation of peroxides, the rate was also a straight line function of peroxide concentration. This, together with other chemical and kinetic evidences, suggested that the peroxides were the catalytic agents responsible for the autocatalytic character of the oxidation reactions.

Detailed rate measurements at very low peroxide concentrations were not made, but extrapolation of the straight line relationship found at higher peroxide concentrations led to a slight positive rate intercept at zero peroxide concentration. More recent studies in the same laboratories have revealed that a

straight line extrapolation of the rate curve is not justified and that the rate of oxidation may indeed be zero at zero peroxide concentration.

Third, it was found that the rate of oxidation was dependent on oxygen pressure. At low oxygen pressures the rate was approximately proportional to pressure, and at higher pressures the rate was virtually independent of pressure. In the case of ethyl linoleate the rate was independent at pressures greater than 150 mm. of mercury, that is, at pressures greater than that of oxygen in air at ordinary atmospheric pressure.

The relationship between rate and oxygen pressure could be expressed as follows:

$$-\frac{d[O_2]}{dt} = k_a \frac{[O_2]}{[O_2] - k_b[RH]} \quad (1)$$

where $[O_2]$ represents oxygen concentration or pressure, $[RH]$ represents linoleate concentration, and k_a and k_b are constants.

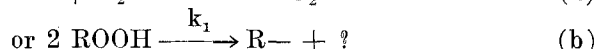
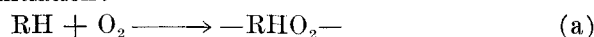
When all of the factors affecting rate are combined, an experimental rate equation is obtained as follows:

$$-\frac{d[O_2]}{dt} = \frac{d[ROOH]}{dt} = k \frac{[ROOH][RH][O_2]}{[O_2] - k_b[RH] + f([O_2], [RH])} \quad (2)$$

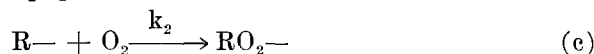
where $[ROOH]$ represents hydroperoxide concentration.

By analogy with other autoxidation reactions, and on the basis of the previously obtained chemical data and these kinetic observations, Bolland and his co-workers proposed the following free radical chain mechanism for the autoxidation of fatty acid esters:

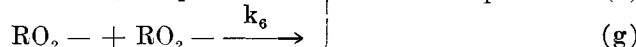
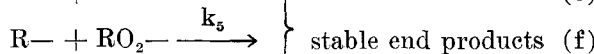
Initiation:



Propagation:



Termination:



In the foregoing sequence the principal chain initiation reaction involves the decomposition of previously formed hydroperoxides by a second order process. It is well known that peroxide decomposition plays an important role in the catalysis of polymerization and other reactions. The mechanisms of decomposition, and the chemistry of peroxides in general, have recently been summarized by Tobolsky and Mesrobian.³

Because extrapolation of the rate curve to zero peroxide concentration gave a slight positive rate intercept at zero peroxide concentration, it appeared necessary to postulate that initially free radicals could

³Tobolsky and Mesrobian, "Organic Peroxides," Interscience Publishers, Inc., New York, 1954.

be formed by direct reaction between oxygen and linoleate. Whether or not such a reaction plays any appreciable role in the very earliest stages of the autoxidation is, in some respects, relatively unimportant because as soon as some peroxide has formed, the peroxide decomposition reaction becomes the main chain initiating reaction.

The chain termination reactions can be justified in several ways. First, since the rate of the chain initiation reaction is proportional to the square of the peroxide concentration and the over-all rate of reaction is proportional only to the first power of the peroxide concentration, it is necessary that the reaction chains be finite in length and further that their average length be proportional to the inverse first power of the peroxide concentration. Second, if free radicals are to be destroyed, it is necessary on chemical grounds that they be destroyed in pairs. Third, it has been found that small amounts of dimeric products are formed during the autoxidation of linoleates, and dimeric products would be anticipated from the interaction of pairs of free radicals as shown in the proposed chain termination reactions.

In the proposed reaction sequence it would be anticipated on the basis of mass action principles that the ratio of $[R-]$ to $[RO_2-]$ would be large when the oxygen concentration is low and therefore that the reaction chains would be terminated primarily by reaction (e). Assuming that reaction (e) predominates, it is possible to establish a theoretical rate equation from the proposed reaction sequence on the basis of mass action principles which agrees with the experimentally derived equation (2), when the oxygen pressure is low. Similarly, when the oxygen pressure is high, it would be anticipated that the ratio of $[RO_2-]$ to $[R-]$ would be large, and that the reaction chains would be terminated primarily by reaction (g). In this case the theoretical rate equation is entirely consistent with the experimental rate equation that pertains when the oxygen concentration is high.

In addition to the kinetic data, various chemical and thermochemical data are in complete accord with the proposed reaction mechanism insofar as its major features are concerned. There are some details of the proposed mechanism however that require further elucidation.

Peroxide Decomposition

Because of the importance of peroxide decomposition reactions in relation to autoxidation, it is worthwhile to consider the peroxide decomposition reactions in slightly greater detail.

Bateman and co-workers have studied the decomposition of cyclohexenyl hydroperoxide in the presence of unoxidized cyclohexene and have found that at higher peroxide concentrations the decomposition occurs *via* a chain mechanism which involves reaction of free radicals with unoxidized cyclohexene. The chain initiation reaction in this case is a second order process, but the over-all order of the decomposition reaction is 1.77, due to the chain nature of the reaction and to the fact that unoxidized cyclohexene is involved.

It was found further that at low peroxide concentrations the over-all reaction rate conformed to a first order process, and it was postulated that the change from a first to second order process as higher perox-

ide concentrations were reached was due to an association of peroxide molecules into dimer particles at the higher concentrations.

In other studies in the same laboratory the rate of autoxidation of ethyl linoleate at very low levels of oxidation was studied in greater detail. It was found that, at very low peroxide concentrations, the autoxidation reaction was not consistent with a second order decomposition of peroxides. It was therefore implied that, perhaps at low peroxide concentrations, the decomposition of linoleate peroxides also does not conform to a second order process.

In recent studies at the Hormel Institute it has been found that linoleate peroxides in low concentrations in unoxidized linoleate decompose by a first order process, and at higher peroxide concentrations the reaction kinetics for the over-all decomposition reaction conform to a second order process. It was also found that unoxidized linoleate does not participate to any appreciable extent in the peroxide decomposition reactions. It is still a moot question however whether the transition from first order to second order kinetics in going to higher peroxide levels can be accounted for on the basis of an association of hydroperoxide molecules into dimer particles, and further whether the latter hypothesis can account for the observed rate characteristics of the linoleate oxidation at low peroxide concentrations.

Pro-oxidants

It has long been known that the autoxidation of fats may be markedly accelerated by various materials. Among the more effective positive catalysts, or prooxidants, are various metals or metallic soaps and salts. Soaps or salts of copper, iron, and cobalt are particularly effective at low concentrations. The acceleration of autoxidation by traces of metals is extremely important not only in relation to the problem of rancidity in food fats but also in the drying of protective coatings. One of the principal functions of driers, such as cobalt and manganese naphthenates, which are added to paints, is to accelerate the oxidation and thereby promote oxidative polymerization.

It now appears to be well established also that a principal mechanism by which metals act as positive catalysts in autoxidation involves their catalytic effect on the decomposition of peroxides. In this mechanism there is no alteration in the basic mechanism involved in autoxidation but merely an alteration in rate. However some metals, in addition to catalyzing peroxide decomposition, enter into the oxidation and subsequent polymerization reactions in other ways that have not yet been completely elucidated, and thus in such cases changes in the mechanisms may be involved.

Light also accelerates the decomposition of peroxides and thereby accelerates autoxidation without however altering the autoxidation mechanisms.

An interesting type of biological catalyst which accelerates the oxidation of fats is the enzyme lipoxidase. Thus far this enzyme has been found only in vegetable materials, notably legumes. Soybeans are one of the best known sources. Lipoxidase accelerates very markedly the oxidation of fats that contain common polyunsaturated fatty acids but has little effect on the rate of oxidation of esters of saturated or oleic acids, or of acids that contain conjugated double bond systems. The enzyme appears to be effective prin-

cipally in the oxidation of substances that contain the 1 *cis*, 4 *cis* pentadiene system.

As in autoxidation, the primary products of the lipoxidase catalyzed oxidation of linoleates are hydroperoxides. There are some differences in the products however that suggest that the mechanism of oxidation is also different. It has been shown that lipoxidase is a typical enzyme, in most respects, and that the kinetics of lipoxidase-catalyzed oxidations resemble in many ways the kinetics of other enzyme reactions. The observations that there are differences in the structures of the peroxides, and in the kinetics of their formation, suggest that the lipoxidase-catalyzed oxidation is not a chain reaction, at least not of the same type that is involved in ordinary autoxidation.

Efforts have been made to derive new chemical products from fats on the basis of lipoxidase-catalyzed oxidations, but at yet such processes are not commercially feasible.

Another type of catalyzed oxidation that appears to have somewhat greater commercial potential involves the use of photochemical pigments, such as chlorophyll. Unsaturated fatty acids and esters, including oleates, may be very rapidly oxidized by atmospheric oxygen under proper conditions in the presence of chlorophyll and light. It appears to have been definitely established in this case that the mechanisms are different than those of ordinary autoxidation.

There are several evidences in support of this view. First, the amount of oxidation that takes place is directly proportional to the amount of light absorbed, and with monochromatic light of wavelength 660 m μ the quantum yield at ordinary temperatures in the case of oleates and linoleates is about 0.1. Second, when mixtures of oleate and linoleate are oxidized, both types of esters are oxidized at comparable rates whereas in autoxidation linoleate is preferentially oxidized. Third, the photochemical oxidation with chlorophyll is not appreciably inhibited by antioxidants. Fourth, it has been found that in the photochlorophyll oxidation of linoleates, appreciable quantities of unconjugated hydroperoxides are formed. Finally, studies of the reaction in intermittent radiation have established that there is no dark reaction such as is found in various other photochemical reactions. Some of these observations are consistent with a conclusion that no chain reaction is involved in this type of oxidation.

The fact that conditions may be selected under which oleate and linoleate in mixtures will be oxidized almost non-selectively appears to make the photochemical oxidation with chlorophyll more attractive than either ordinary autoxidation or lipoxidase-catalyzed oxidation for the development of new products for some applications, assuming that the process can be made commercially feasible.

Antioxidants

There are also various substances that have a marked retarding effect on the autoxidation of fats and oils, and such materials are known as antioxidants. Much effort has been devoted to searches for new and better antioxidants, and to studies of the mechanisms whereby antioxidants exert their effects, because of their importance to the prevention of rancidity in food fats. Among the most effective so-called primary antioxidants are various polyphenols and

aromatic amines. Compounds of the latter class however are generally considered too toxic for food use. The most important commercial primary antioxidants therefore are phenolic in character.

Phenolic antioxidants exert their retarding effect on autoxidation primarily by breaking the reaction chains. This they do by acting as free radical acceptors. In the case of dihydric phenols, one antioxidant molecule is capable of destroying two free radicals and is converted to a quinone in the process. Under some conditions the destruction of two free radicals may prevent the formation of hundreds of molecules of hydroperoxide.

There are some types of materials that are classified as antioxidants that are not highly effective by themselves as antioxidants but, when added in combination with a primary antioxidant, may markedly enhance the effectiveness of the latter. Such secondary antioxidants are sometimes called synergists. Included in this category are such substances as phosphoric acid, citric acid, isopropyl citrate, ascorbyl palmitate, and various organic hydroxy acids.

Some of these substances are good chelating agents for metallic ions, and their synergistic effect may be attributed in part at least to their inactivation of metallic prooxidants that are present adventitiously in fats. Some investigators hold that this is the only mechanism of synergism in antioxidation. Other investigators feel however that synergism may involve other mechanisms also. It has been proposed, for example, that in some cases the synergistic antioxidant catalyzes a reduction of the oxidized antioxidant back to its original reduced state. Unequivocal confirmatory evidence for this mechanism however has not yet been obtained. Still another possibility is that secondary antioxidants react with hydroperoxides by some mechanism which does not involve free radical production. Reactions of this character would thereby counteract the prooxidant effect of the peroxides themselves.

Phenolic antioxidants show an interesting peculiarity in that they exert a prooxidant effect as well as an antioxidant effect. They greatly prolong the so-called induction period of fats but at the same time accelerate the rate of peroxide formation during the induction period. The prooxidant effect appears to be attributable to a catalytic effect of the antioxidant on decomposition of peroxides. More reaction chains are thereby started, but at the same time the antioxidant also greatly reduces the length of the reaction chains so that the over-all effect is a prevention of any rapid rate of autoxidation until such time as all of the antioxidant is destroyed. On this basis it has been proposed by some investigators that a synergistic antioxidant exerts its effect by interfering with the prooxidant effect of primary antioxidants, without at the same time affecting their antioxidant or chain breaking effect.

Autoxidation in Relation to Unsaturation

It has already been indicated that in mixtures of compounds having different degrees of unsaturation, the more unsaturated compounds are preferentially oxidized in ordinary autoxidation. In general, the rate of oxidation in pure individual fatty acid esters also increases with increasing unsaturation. This appears to be due, in part at least, to a greater instability of the peroxides of the more unsaturated

compounds. Oleate peroxides are relatively stable; linoleate peroxides and, even more so, linolenate peroxides decompose quite rapidly even at ordinary temperatures.

It should be mentioned also that there appear to be some structural differences in the types of peroxides formed in compounds with different degrees of unsaturation although in all cases, except in conjugated systems, the predominant peroxides are hydroperoxides. In the case of oleates however, peroxide analyses by polarographic methods usually show a hydroperoxide content that is lower than the peroxide content found by iodometric methods of analysis. These observations suggest that perhaps some cyclic peroxide may be formed by direct addition of oxygen at the double bonds in the case of oleate. In the case of linoleates, on the other hand, initial products are virtually wholly hydroperoxides; some non-peroxidic materials are also formed concurrently with peroxide formation.

In the case of linolenates there is some disagreement about the nature of the products. Some workers have found that relatively small proportions of hydroperoxides are formed and that large proportions of the secondary products are found at all stages of the oxidation. More recent work has indicated however that even with linolenates under sufficiently mild conditions of oxidation, the predominant products formed initially are hydroperoxides. Because of the instability of the peroxides however various secondary reactions occur quite early in the oxidation so that many secondary products including different types of peroxidic materials are rapidly formed. In this case, also, some of the early products of oxidation are unsaturated aldehydes which appear to be partly or wholly responsible for the so-called "reverted" flavors that develop in fats that contain linolenic acid.

In the case of conjugated polyunsaturated fatty acid derivatives, oxidation occurs by a somewhat different mechanism. It is generally accepted that in conjugated systems, a considerable proportion of cyclic peroxides is formed, presumably by a 1,4 addition of oxygen. Other aspects of the autoxidation of conjugated derivatives have not been extensively studied.

Secondary Products

With most fats and oils autoxidation does not proceed very far before considerable proportions of secondary products develop. Even in the initial stages of autoxidation a small proportion of these is formed concurrently with the peroxides. For the most part however the secondary products are formed by a decomposition of the peroxides, by interaction of the

peroxides with other materials in the autoxidizing fat, and by further oxidation of the peroxides. A wide variety of materials may thus be formed, including various aldehydes, ketones, acids, hydrocarbons, carbon dioxide, carbon monoxide, hydrogen, hydrocarbons, and various other substances.

On the basis of present knowledge of organic reactions, some of the secondary products of autoxidation of fats are quite unexpected, and little is known about the mechanisms by which they are formed. Further studies of the nature of the secondary products of oxidation and of the mechanisms of their formation appear to have great potential value. On the basis of information obtained in such studies, it may be possible to control autoxidation reactions in a way that will enhance the production of certain desired products with potential or actual commercial value.

A large and heterogeneous class of secondary products that are important insofar as present applications of fats and oils are concerned are the polymers formed in the drying of oils used in protective coatings and printing inks. As already indicated, polyunsaturated fatty acid esters in the process of peroxide formations form conjugated systems. These may polymerize by any one of a number of reaction mechanisms. Moreover the peroxide groups through their decomposition catalyze such polymerizations. Much remains to be learned about the mechanisms of the polymerization processes and the structures of the polymeric products formed.

On the basis of recent researches there are promising possibilities for the development of new products from inedible fats by autoxidation. The possible use of catalysts, such as chlorophyll and lipoxidase, has been mentioned. Various other catalysts remain to be investigated. Moreover it has been found that the products of autoxidation can be separated by counter-current distribution techniques employing diphasic liquid systems. Further development of these techniques may aid in establishing the economic feasibility of new products from fats through autoxidation.

Still another fruitful field for investigation is the autoxidation of fats at higher temperatures, possibly even in a vapor state, using specialized catalysts such as have been developed for converting petroleum hydrocarbons to desired products by oxidation. Virtually no work on the development of such processes for fatty materials is reported in the literature. With the present economic tendency toward over-supply of fats and oils, particularly animal fats, it is reasonable to suppose that the next 10 years will see the initiation of many interesting researches designed to develop new industrial chemicals from fats by autoxidation processes.