

## Autoxidation of Saturated Fatty Acids. A Review

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Saturated fatty acids and their esters are known to undergo thermal oxidation. Farmer's hydroperoxide theory is, however, not applicable for these compounds. Several theories regarding the products and location of the initial oxidative attack are briefly reviewed. Recent work identifying monohydroperoxides as the initial products of autoxidation of methyl palmitate is described in some detail.

The oxidation does not occur selectively at a single location along the ester and does not require the presence of unsaturation in the molecules. The effect of purity and temperature on the products of autoxidation of saturated fatty acids and its possible implications of these reactions for flavor chemistry are also discussed.

The reactions that take place between lipids and atmospheric oxygen are usually referred to as autoxidation. Autoxidation of commercial fats is most commonly an autocatalytic process. Light, heat, enzymes, concentration of oxygen, moisture, and chemical prooxidants or antioxidants affect its rate.

Animal fats such as those found in dairy products and meat usually contain 40% of saturated fatty acids, yet, because of their relative stability, their contribution to the deterioration of foodstuffs has usually been considered insignificant. Consequently, most of the research interest in the field of lipid oxidation has been devoted to the study of the reactions in unsaturated fatty acids.

Saturated fatty acids are chemically paraffin derivatives and can be considered hydrocarbons with a terminal carboxylic group. Because of the interest of the petroleum industry in the products of alkane oxidation, these reactions have been studied in great detail. Catalysts and cracking temperatures have been used in most of these experiments. However, catalyzed oxidation of fats and chemical oxidation by reagents other than atmospheric oxygen result in rapid reactions, leading to the formation of complex end products, usually accompanied by the disappearance of most of the intermediary products.

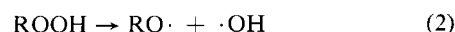
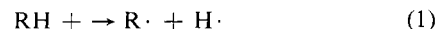
Considerable interest has developed in autocatalytic oxidation of saturated fatty acids in recent years, resulting in preliminary information regarding its mechanism. Some of the factors that affect the mechanism and products of autoxidation of saturated fatty acids are the subject of this review.

### FACTORS AFFECTING RATE OF AUTOXIDATION

The free radical chain theory postulated by Farmer and his coworkers (1943) has been generally accepted as an explanation of the mechanism of autoxidation of unsaturated lipids. Three distinct stages can be identified in this process: initiation, propagation, and termination. A free radical,  $R\cdot$ , may be produced initially by heat, light, or radiation. Thermal initiation involves molecular oxygen. The free radicals react rapidly with oxygen to form a peroxy radical,  $ROO\cdot$ . The peroxy radical extracts hydrogen from another molecule, forming a hydroperoxide,  $ROOH$ , and a new free radical,  $R\cdot$ .

The initiation step is the least understood part of the autoxidative process and its effect is difficult to separate from propagation once the reaction has begun.

Thermal initiation may occur as a result of the following reactions:



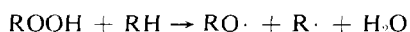
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Reaction 1 requires 30 to 45 kcal. per mole for saturated hydrocarbons, against only 20 to 35 kcal. per mole for Reaction 2 and even less for Reaction 3 (Ingold, 1961). Hence, in the presence of even a trace of hydroperoxide, the lower endothermicity would favor decomposition of peroxides, according to Reaction 2, leading to formation of free radicals. The free radicals react with molecular oxygen and with other hydrocarbons, leading to scission and the formation of secondary oxidation products, as well as new free radicals (Knorre *et al.*, 1958). The presence of compounds that catalyze the decomposition of peroxides also tends to accelerate the rate of autoxidation and, hence, has a pro-oxygenic effect on the reaction.

The endothermicity of Reaction 1 varies in accordance with the strength of the R—H bond of the substrate. Presence of unsaturation, branching, or other factors that weaken the carbon-hydrogen bonds in the substrate increases the rate of thermal initiation.

Sturton *et al.* (1945) demonstrated the effect of unsaturation on autoxidation. At 100° C., the methyl esters of linolenic, linoleic, oleic, and stearic acids oxidized at a rate of 179:114:11:1, respectively. Moreover, they demonstrated that the iodine number is not a reliable index of stability toward autoxidation. Mixtures of methyl linoleate and methyl stearate absorbed oxygen considerably faster than methyl oleate of the identical iodine number.

Reactions that lead to formation of more free radicals accelerate the rate of autoxidation. Such a reaction is the bimolecular interaction of a hydroperoxide with a hydrocarbon:



Maizus *et al.* (1960) demonstrated that the rate of this reaction is increased by substituting for *n*-decane compounds possessing C—H bonds with lower dissociation energies. The order of reactivity increased from *n*-decane to isodecane to ethylbenzene to methyl oleate.

Other factors also affect the reactivity of fatty acids. Arndt *et al.* (1959) studied the effect of a methyl group on the position of radical attack during autoxidation of 5-methylnonane at 90° C. The order of susceptibility was found to increase from primary to secondary to tertiary carbons. Hydrogen was removed four times more readily from a secondary carbon than from a primary one, and 19 times more readily from a tertiary than from a secondary one. Based on extensive studies of the oxidation of lubricating oils, Zuidema (1946) concluded that branched paraffins probably oxidize at the point of branching as well as at the beta carbon.

Similarly, Maizus *et al.* (1960) showed that isodecane has a higher reaction constant than *n*-decane. Results of George *et al.* (1946) (Table I) indicate that the rate of oxygen uptake (moles of O<sub>2</sub> per mole per hour) during oxidation of alkane derivatives at 110° C. is affected by the structure of the substrate. These researchers also found that carbonyls are more readily oxidized than either saturated fatty acids or paraffins, while alcohols generally are more stable to autoxidation.

The stability of saturated fatty acids toward autoxidation decreases with increased chain length. Nobori (1942) found that lauric acid scarcely was affected by oxidation at

Table I. Oxidation Rates of Some Hydrocarbon Derivatives<sup>a</sup>

Compound	Structure	Oxidation Rate, (Moles O <sub>2</sub> per Mole per Hour)	
		Uncatalyzed	Catalyzed
2-Octanol	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>5</sub> CHOHCH <sub>3</sub>	0.06	0.2
1-Hexadecanol	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>14</sub> CH <sub>2</sub> OH	0.08	0.8
Long-chain			
<i>n</i> -paraffin	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> CH <sub>3</sub>	0.25	4.8
Stearic acid	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>16</sub> COOH	0.50	7.3
12-Tricosanone	(C <sub>11</sub> H <sub>23</sub> ) <sub>2</sub> CO	2.6	8.6
Enanthaldehyde	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>5</sub> CHO	720.0	55.0

<sup>a</sup> After George *et al.* (1946).

150° C. in the presence of 0.1% KMnO<sub>4</sub>. Under the same conditions stearic acid was broken down to lower fatty acids, to lactones, and to other products which contain hydroxyl groups. Other workers also concluded that stability decreased as the chain length increased under catalyzed (Nobori and Noguchi, 1943; Paquot and de Goursac, 1950) as well as autocatalytic conditions (Nataka, 1954; Ramanathan *et al.*, 1959).

The rate of chemical reactions is dependent on both the concentration of the reactants and the temperature and pressure under which they interact. During the initial stages of autoxidation, fatty acids or their esters are available in great abundance. Under these conditions, low concentrations of oxygen might limit the rate and extent of the reaction. During thermal oxidation of corn oil, Johnson and Kummerow (1957) noted that an increase in the rate of aeration resulted in a greater magnitude of the changes while not altering the over-all reaction.

Pyrolysis occurs at temperatures about 600° C., leading to the production of paraffins and olefins (Bailey and Turek, 1956). Thermal cracking requires considerably more energy than the thermal initiation of autoxidation (70 to 100 *vs.* 30 to 45 kcal. per mole) (Ingold, 1961). Cracking, therefore, does not occur to any measurable extent under autocatalytic conditions at atmospheric pressure. Hrdlicka and Pokorny (1962) found that high temperature greatly favored the formation of unsaturated volatiles during autoxidation of stearic, oleic, erucic, and linoleic acids. The scission of the carbon-carbon chains at 180° C. occurred at approximately the same places as at lower temperatures, but, at elevated temperatures was not limited to the double bond (Hrdlicka and Pokorny, 1963). Formation of unsaturation by the attack of oxygen at elevated temperatures was suggested to be the initial step in the autoxidation of saturated fatty acids (Ramanathan *et al.*, 1959).

#### INITIAL PRODUCTS OF AUTOXIDATION

Oxidation of model systems consisting only of saturated lipids with the aid of metal catalysts or at a temperature of 180° to 200° C., results in complex mixtures of carbonyl, hydroxyl, and carboxyl compounds. Hrdlicka and Pokorny (1962) identified 10 volatile aldehydes as products of autoxidation when stearic acid was heated for 150 minutes to 180° C. Oxidation of stearic acid at 100° to 120° C.

in the presence of a metal catalyst was shown by Paquot and de Goursac (1950) to lead to the formation of all members of the even-numbered series of acids from acetic to palmitic, as well as small amounts of lactones. Complex mixtures of mono- and dibasic acids, aldehydes, and ketones were reported in oxidized saturated lipids (Crossley *et al.*, 1962, Thaler and Saumweber, 1961a,b). These are all secondary products of the oxidative attack.

Analysis of the products of thermal oxidation of methyl laurate, methyl stearate, and tripalmitate at 200° C. in a stream of air led Ramanathan *et al.* (1959) and Endres *et al.* (1962a,b) to conclude that dehydrogenation was the initial step in the reaction. The resultant unsaturated molecules then were believed to have oxidized with the formation of hydroperoxides, although no measurable concentrations of the peroxides were obtained. The peroxides then decomposed instantaneously to form the various secondary products of autoxidation. Brodnitz *et al.* (1968b) recently attempted to detect the presence of unsaturation in methyl palmitate oxidized at 150° C. On microhydrogenation, a sample containing 1 mmole of oxidized methyl palmitate absorbed less than 0.01 mmole of hydrogen, indicating no measurable unsaturation in the oxidized molecules. The formation of a free radical rather than unsaturation therefore is probably the initial step in the autoxidation of saturated fatty acids at 150° C.

The formation of hydroperoxides as the initial stable products of oxidation of saturated fatty acids and their esters has been postulated, but little information regarding the nature of these hydroperoxides has been gained. Stirton *et al.* (1945) noted that methyl stearate with an iodine number of 0 absorbed oxygen at a slow rate at 100° C. The course of peroxide accumulation during oxidation at 120° and 150° C. of lauric and stearic acids and their methyl esters was followed iodometrically by Thaler and Saumweber (1961a). Peroxide accumulation in these lipids during oxidation at 150° C. proceeded at a steady rate until a maximal level was reached in less than 5 hours, before rapidly decreasing and leveling off at a lower value. The observed pattern closely resembled that observed by Knight *et al.* (1951) for methyl oleate. The maximal peroxide level during oxidation of methyl palmitate at 150° C. is attained at a time when more than 50% of the unoxidized ester is still present (Brodnitz, 1966). While the phenomenon of maximal peroxide values is similar to that noted by Coleman *et al.* (1955) for methyl oleate, the depletion of substrate observed by them cannot be offered as its explanation.

The apparent similarity between saturated hydrocarbons and saturated fatty acids has led to the suggestion that the results of the former could be applied to the latter. Studies of George *et al.* (1946), for example, could be cited as evidence that hydroperoxides were the primary products of autoxidation of saturated lipids. These studies, however, were based heavily on oxygen uptake data and iodometric determinations of the peroxides formed. Neither of these methods is specific for hydroperoxides. Zuidema (1946) postulated that the initial product of alkane oxidation at 100° to 200° C. was a monohydroperoxide. Twigg (1954) reduced the peroxides formed during the autoxidation of *n*-decane at 145° C. to the corresponding alcohols by use of palladium black. Alumina chromatography of

the reduced products indicated that about 10% of the molecules were attacked twice. The proportion of dihydroperoxides and diketones was considerably higher than expected statistically if each attack on a molecule was made separately.

Multiple oxidative attacks also have been demonstrated on unsaturated fatty acids. Recently, Begemann *et al.* (1967) reported that a mixture of diperoxides, consisting of a cyclic peroxy and a hydroperoxy group found together on the same molecule, accounts for 35% of the peroxides formed by mild autoxidation of methyl linolenate. Studies on the nature of the peroxides formed during the autoxidation of saturated fatty acids indicate, however, that monohydroperoxides are the initial stable products of that reaction.

Methyl palmitate of purity greater than 99.99% and free of all detectable unsaturation, peroxides, or other measurable impurities was autoxidized in the dark at 60°, 150°, and 200° C. (Brodnitz *et al.*, 1968a). After 8 weeks of oxidation at 60° C., no peroxides were detected in the highly purified ester. However, oxidation at 150° C. resulted in the accumulation of over 600 meq. of peroxides per kg. in 3 hours. Polarographic analysis of the oxidized methyl palmitate indicated the presence of a major wave with a half-wave potential within the reducing range for hydroperoxides and a minor wave due to secondary products of oxidation. Following reduction of the oxidized ester with sodium borohydride, the characteristic hydroperoxide wave did not appear on the polarograph. Gas chromatographic analysis of the reduced samples revealed the presence of a single major peak. Infrared and mass spectroscopy indicated that this peak was the methyl ester of hydroxypalmitic acid. The absence of dihydroxy esters in the reduced samples provides additional evidence that the initial attack results in the formation of monofunctional compounds.

Thin-layer chromatography experiments revealed that the major product of autoxidation of highly purified methyl palmitate had a retention factor identical to that of monohydroperoxides of oxidized methyl oleate and methyl palmitoleate. No indications of the presence of difunctional compounds were found in the oxidized esters. Minute concentrations of free radicals are sufficient to initiate the autoxidation of methyl palmitate even at 60° C. Purified methyl palmitate free of all detectable unsaturation or peroxides was oxidized at 60° C. for 8 weeks without formation of any hydroperoxides that could be detected by TLC. Thin-layer chromatography of a duplicate sample of 99.5% pure methyl palmitate, also free of all detectable unsaturation or peroxides, revealed the formation of hydroperoxides after 20 days of oxidation. The addition of 5% by weight of either lauroyl peroxide (97%) or methyl linoleate (99%) to the 99.5% pure ester led to the formation of measurable amounts of hydroperoxides in the saturated ester within 6 days of autoxidation.

Hilditch (1950) reviewed the experimental conditions under which methyl oleate has been oxidized. He suggested that below 50° C. a monounsaturated system is not susceptible to direct attack by oxygen. Based on the results of Brodnitz *et al.* summarized above, a similar conclusion seems to apply to saturated esters. These esters apparently can undergo a propagation reaction, but not

thermal initiation during storage in the dark at 60° C. At 150° C., the initiation reaction of the autoxidation of highly purified methyl palmitate occurs readily. The extent of oxidation of this ester, measured by the iodometric peroxide method, was at least as large as that noted for a sample of 99.5% methyl palmitate, suggesting that the presence of pro-oxygenic impurities in the less pure ester did not measurably accelerate this reaction.

No peroxides have been isolated as products of thermal oxidation of saturated lipids at temperatures above 190° C. (Brodnitz *et al.*, 1968a; Crossley *et al.*, 1962; Endres *et al.*, 1962a,b; Ramanathan *et al.*, 1959).

Hence, monohydroperoxides are shown to be the initial stable products of autoxidation of esters of saturated fatty acids. The maximal accumulation of peroxides is observable in samples oxidized at 100° to 150° C.

#### POSITION OF INITIAL ATTACK DURING AUTOXIDATION OF FATTY ACIDS

The presence of unsaturation, carbonyl, or secondary methylene groups in a molecule has been shown to result in a highly specific autoxidative attack. In the absence of such a reactive site in the molecule, several suggestions regarding the position of the oxidative attack have been made.

The first of the recent studies of the autoxidation of methyl esters of saturated fatty acids at atmospheric pressure was conducted by Ramanathan *et al.* (1959). Pure fatty acids were obtained by crystallization from acetone, methylated, and fractionally distilled in vacuo. The methyl esters of lauric, stearic, and oleic acids were then oxidized at 200° C. by dry oxygen for periods up to 16 hours. Condensable volatile decomposition products were collected in two traps maintained at -80° C. The weights of the noncondensable products—hydrogen, carbon dioxide, and carbon monoxide—were also determined.

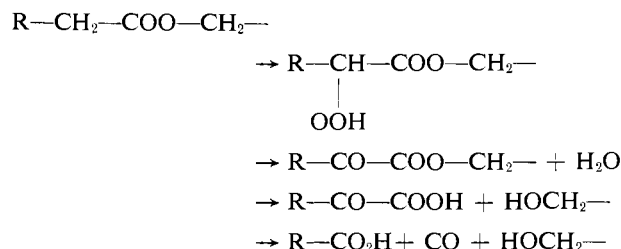
Propionic, butyric, valeric, and caproic acid were detected (in the condensable products of methyl laurate oxidation) after 1 hour. Acetic acid was first noted after 4 hours of oxidation. On oxidation of methyl stearate, only nonanoic acid was detected by paper chromatography after 1 hour of oxidation, while acetic, propionic, butyric, valeric, and pelargonic acids were first observed after 4 hours. Pelargonic acid also was identified as the major product of methyl oleate oxidation. The presence of nonanoic acid at the end of 1 hour of oxidation in methyl stearate indicates that the C—C linkage between carbons 9 and 10 is especially susceptible to oxidation. This susceptibility was ascribed to dehydrogenation of the methyl stearate as suggested by the evolution of hydrogen and the increase in the apparent iodine values of the esters during the thermal oxidation. Acetic and caproic acids were postulated to be the products of secondary oxidative attacks on pelargonic acid.

The relative stability toward oxidative decarboxylation by molecular oxygen of a homologous series of saturated acids was studied by Makalets (1960). Acetic to caproic acids, with <sup>14</sup>C in the carboxyl group, were autoxidized at 142° C. under 6 atm. for 3 hours, and the production of CO<sub>2</sub> was followed. The oxidation rates from propionic to caproic acid were practically identical and consequently did not depend on the length of the chain. Acetic acid

oxidized to a markedly smaller extent under the same conditions. The results suggested that saturated acids are oxidized through an attack at the C—H bond of the alpha-CH<sub>2</sub> group. Acetic acid contains a more stable methyl group at the alpha position, and is therefore less susceptible to oxidation.

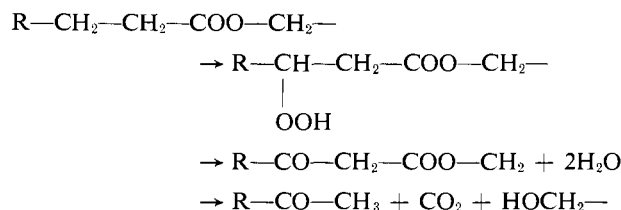
Paquot and de Goursac (1950) noted that when saturated fatty acids were oxidized in the presence of 1% nickel phthalocyanine, at 100° to 120° C., all the members of the series of even-numbered acids from acetic and up were formed. Methyl ketones of odd-numbered carbons and oxalic acid were found in all oxidation products. From these results, too, it appears that the major attack occurs by beta-oxidation. The presence of small amounts of lactones in the oxidation products suggests that some gamma or delta oxidation also took place.

Crossley *et al.* (1962) oxidized tricaprin in a slow stream of dry air at 190° C. In addition to capric acid, pelargonic, caprylic, enanthic, caproic, valeric, and traces of lower acids were formed. Several methyl ketones also were found in the oxidized product, the major one being methyl *n*-heptyl ketone. Methyl *n*-octyl, methyl *n*-hexyl, and di-*n*-amyl ketones, and traces of *n*-decanal also were present. No dibasic acids were detected during the oxidation of tricaprin. From these products Crossley *et al.* (1962) judged that the dominant attack was on the alpha carbon atom of the acid, leading to the following sequence of reactions:



This initial reaction leads to the formation of pelargonic acid, which by further oxidation, leads to the formation of the shorter acids.

Beta oxidation is suggested to explain the formation of the methyl ketones:



Methyl *n*-heptyl ketone would result from these reactions if tricaprin was the initial compound. Other methyl ketones could result from beta oxidation of the lower homologs obtained through alpha oxidation.

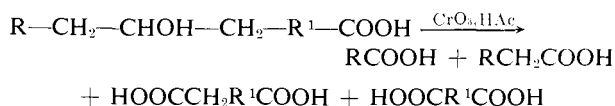
Qualitative analyses of the volatile decomposition products of autoxidation of lauric and stearic acids at 150° C., by Thaler and Saumweber (1961a,b), showed the presence of all the saturated normal acids and aldehydes from C<sub>1</sub> to C<sub>6</sub>. By paper chromatography, the formation of C<sub>12</sub>, C<sub>13</sub>, C<sub>14</sub>, C<sub>15</sub>, and C<sub>16</sub> saturated acids during the oxidation of both stearic acid and its methyl ester was established.

The even-numbered acids were present in substantial quantities. However, only traces of C<sub>15</sub> and C<sub>13</sub> acids were detected, and no indication of the presence of heptadecanoic acid was found. Undecylic acid, however, was detected in the products of autoxidized lauric acid and its ester. All the dibasic acids from oxalic through sebacic acid, except malonic acid, were also found. The absence of malonic acid is probably due to its instability at 150° C.

The determination of the position of the initial radical attack during autoxidation of saturated fatty acids from the products of oxidation is, at best, difficult. A more direct approach, such as the one used by Benton and Wirth (1953) in the study of *n*-decane oxidation, yields information regarding the location of the oxidative attack. The peroxides formed during the oxidation of *n*-decane were hydrogenated, leading to the formation of a mixture of decan-1-ol and the four secondary decanol isomers. Infrared analysis of the isomers permitted quantitative estimation of the various isomers, and clearly indicated that only a small proportion of the attack occurred at the terminal methyl groups and that the major attack in the paraffin was distributed almost equally on the methylene groups of the *n*-decane.

The location of the attack in saturated fatty acids cannot be quantitatively identified by infrared spectrometry. Instead, concentrated peroxides can be reduced to form the hydroxy derivatives of the esters. Chromium trioxide dissolved in acetic acid cleaves hydroxymethyl esters preferentially at the carbon to which the hydroxy group is attached (Meakins and Swindells, 1959).

Two mono- and two dibasic acids are obtained on oxidation of a molecule containing a single hydroxy group in the middle of the ester. This reaction can be presented in the following general form:



The hydroxymethyl esters also can be oxidized to the keto esters, converted into oximes, and subjected to the Beckmann transformation method of Christie *et al.*, forming a hydroxy ester (1963). Unlike the oxidation with chromium trioxide, only a single mono- and a single dibasic acid are formed by the hydrolysis of the amide obtained from the hydroxy ester (Christie *et al.*, 1963; Ross *et al.*, 1949).

These methods of analysis, as well as nuclear magnetic resonance spectroscopy of the hydroxy esters obtained by reducing the peroxides of methyl palmitate oxidized at 150° C., were used in a recent study by Brodnitz *et al.* (1968b). NMR spectroscopy of the reduced esters indicated that, as in an autoxidation of paraffins (Benton and Wirth, 1953), the hydroxy groups were not located at either end of the molecule. Moreover, the probability of preferential beta oxidation was also ruled out by the NMR spectra.

Gas chromatographic analysis of methyl esters obtained by oxidation of the hydroxypalmitates with chromium trioxide was carried out on columns coated with polar and nonpolar liquid phases. Identification of these esters indicates the presence of all the monobasic esters from C<sub>4</sub>

through C<sub>16</sub> and the dibasic esters eight to 12 carbons long, with special concentration toward the middle of the molecule.

#### POSSIBLE IMPLICATION FOR FLAVOR CHEMISTRY

Saturated acids, aldehydes, and *n*-alkan-1-ols have been identified in products of milk and corn lipid oxidation (Day and Lillard, 1960; Kawada *et al.*, 1967; Krishnamurthy and Chang, 1967; Stark and Forss, 1966). Day and Lillard (1960) found that approximately 63% of the monocarbonyls isolated from milk fat were *n*-alkanals. Many of these compounds have been demonstrated by Day *et al.* (1963) and Scanlan *et al.* (1965) to affect the flavor of the lipid at concentrations of less than 1 p.p.m. Lillard and Day (1964) have demonstrated how most of the observed products of oxidation can be theoretically predicted as primary products of the autoxidation of the esters of oleic, linoleic, and linolenic acids or from secondary oxidation of unsaturated aldehydes formed from them. Stark and Forss (1966) suggested recently that several alkanols identified from oxidized butter originated from primary (terminal) hydroperoxides of myristoleate. The studies summarized above suggest, however, that at least part of these saturated compounds might have been formed by autoxidation of saturated fatty acids and their esters.

When lipids are subjected to thermal oxidation, even the most purified saturated esters are readily attacked by molecular oxygen. Above 180° C., the resultant hydroperoxides decompose as soon as they are formed, leading to the formation of saturated aldehydes, semialdehydes, and saturated mono- and dibasic fatty acids. The location of the oxidative attack takes place preferentially toward the center of the molecule but not selectively at a single carbon atom (Brodnitz *et al.*, 1968b). Hence, saturated acids and aldehydes, especially those with five to 12 carbons, could be formed by the oxidation of saturated esters such as palmitate and stearate, which are the major constituents of most natural lipids. The initiation reaction in the autoxidation of pure saturated fatty esters is extremely slow at temperatures of 60° C. or below. Presence of even extremely small amounts of peroxides or unsaturation is enough to supply the free radicals necessary to begin the autoxidative process in these esters (Brodnitz *et al.*, 1968a). In natural lipid systems in which considerable concentrations of autoxidizing unsaturated fatty acids are present, oxidative attack on the saturated ester undoubtedly also takes place. The products of this reaction are relatively low in concentration in comparison with the primary products of oxidation of oleic, linoleic, or linolenic acid. It appears likely, however, that autoxidation of saturated fatty acids leads to the formation of some of the products observed in oxidized lipids. Since the flavor threshold concentration of these saturated aldehydes is often well below the part per million level (Day *et al.*, 1963), their possible contribution to the oxidized flavor should not be ignored.

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