

# Reactions of Fatty Materials with Oxygen. XX.<sup>1</sup> Recent Developments in the Autoxidation of Methyl Oleate and Other Monounsaturated Fatty Materials<sup>2</sup>

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WITHIN THE past 10 years several reviews have been published on the autoxidation of fatty materials (37, 48, 56, 57, 59a, 66). Generally these articles have covered a broad range of subjects, namely, the autoxidation of saturated, monounsaturated, and both conjugated and non-conjugated fatty substances. In part because of the voluminous literature on the subject and in part because of space limitations the reviews have been general and limited largely to high points in the developments of this important field.

From about 1947 to the present there has been considerable research on various phases of the autoxidation of monounsaturated and non-conjugated polyunsaturated fatty esters. The major developments and progress in the field have been the direct outgrowths of the use of modern instruments (polarograph, spectrophotometers, etc.) to study the initial stages of autoxidation, and modern isolation techniques (urea complexes, countercurrent distribution, chromatography, etc.) to separate reaction products, as well as to study the initial stages. Progress within the past decade has been so rapid that a detailed discussion of the present status of the autoxidation of monounsaturated and non-conjugated polyunsaturated esters is warranted.

The purpose of this paper is to survey and critically evaluate significant recent developments in the autoxidation of methyl oleate and other monounsaturated fatty materials, a field in which we have played an active part. This paper will also attempt to integrate various lines of recent research work on methyl oleate carried out in this laboratory and elsewhere.

*Preparation and Characterization of Hydroperoxides.* For about 50 years it was assumed that the autoxidation of unsaturated substances proceeded by direct addition of oxygen to the double bond to yield a cyclic peroxide of some kind. This conclusion was based mainly on analytical evidence, much of which was unreliable or misinterpreted. No ring peroxide has been isolated from the oxidation products of methyl oleate or non-conjugated polyunsaturated compounds.

With the isolation and positive identification of  $\alpha$ -methylene hydroperoxides from cyclohexene and other simple olefins (24, 30, 36) it was quite evident that the earlier theories required revision. A major step forward in clarifying the mechanism of autoxidation of methyl oleate was the isolation of methyl oleate hydroperoxides by Farmer and Sutton (31), who used molecular distillation and also chromatography. Later Swift, Doller, and O'Connor (69) employed low-temperature solvent crystallization to obtain a 90% peroxide concentrate from methyl oleate. More recently Fugger, Zilch, Cannon, and Dutton (33) by

countercurrent distribution, also Privett, Lundberg, and Nickell (52) by a modified extraction procedure have fractionated autoxidized methyl oleate between aqueous ethanol and hydrocarbon solvents and obtained 80–90% peroxide concentrates. Zilch and Dutton (73) also examined numerous model compounds known to be present in autoxidation mixtures. For large scale laboratory preparation Coleman, Knight, and Swern (20) employed the urea complex separation technique to precipitate unoxidized methyl oleate thereby concentrating the hydroperoxides in the filtrate. Hydroperoxide contents of about 90% were consistently obtained if the extent of autoxidation did not exceed 15–20%.

On the basis of manometric measurement of oxygen absorption by methyl oleate and subsequent countercurrent distribution of the autoxidation mixtures, Fugger, Zilch, Cannon, and Dutton (33) obtained evidence that monohydroperoxides are the first stable products in the reaction with gaseous oxygen and that the ethylenic double bond is not attacked until a subsequent oxidation. No evidence of dimer formation was observed.

The availability of substantial quantities of hydroperoxides (90% purity) from methyl oleate permitted a more detailed examination of their characteristics. Swern, Coleman, Knight, Ricciuti, Willits, and Eddy (63), employing the infrared spectrophotometer, showed that most, if not all, of the hydroperoxides formed during the autoxidation of methyl oleate have the *trans* configuration, thus fully substantiating their earlier conclusions which were derived from unfractionated autoxidation mixtures (42). Independent confirmation of this was recently obtained (19a, 40a). Methyl oleate (*cis*) hydroperoxide has undoubtedly never been prepared. The product so named in the literature should be referred to as methyl *trans*-octadecenoate hydroperoxides. A mechanism for the formation of *trans* hydroperoxides from methyl oleate based on the free radical mechanisms of autoxidation has been proposed by Knight, Eddy, and Swern (42).

Furthermore the double bond is not in the original 9,10-position in these hydroperoxides as Ross, Gebhart, and Gerech (53) and others (32, 42) have proven. Based on the available evidence (39a, 42), it has been proposed that the hydroperoxides from autoxidized methyl oleate consist largely of methyl 9-hydroperoxido-*trans*-10-octadecenoate and methyl 10-hydroperoxido-*trans*-8-octadecenoate, but other isomers must also be formed to some extent (53).

Although it has been assumed (tacitly perhaps) that the peroxides from autoxidized methyl oleate are exclusively hydroperoxides, it is extremely doubtful that such is the case. Willits, Ricciuti, Knight, and Swern (70) have shown that polarographic analysis is a convenient and accurate way to determine hydroperoxides in the presence of other peroxide types. Polarographic examination of many peroxide concentrates from autoxidized methyl oleate has shown that,

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although hydroperoxides predominate, as much as 28% of the peroxides may be non-hydroperoxides (63). Polarographic studies of autoxidized methyl oleate and other materials have also been reported by Lewis and Quackenbush (45, 46), Nogami, Matsuda, and Nagasawa (49), Paquot and Mercier (51), and Willits, Ricciuti, Ogg, Morris, and Riemenschneider (71).

The structure of these non-hydroperoxides is still unknown. It is possible that they may be the cyclic peroxides which earlier workers proposed. The fact that reduced peroxide concentrates show an  $\alpha$ -glycol content substantially equal to the original non-hydroperoxide content has been offered as evidence that cyclic peroxides are formed (63). Until they are isolated however, the evidence must be regarded as circumstantial particularly since  $\alpha$ -ketols have been reported as components of the autoxidation mixture and these are also readily reduced to  $\alpha$ -glycols (40a).

**Mechanism of Autoxidation.** The facile formation of hydroperoxides from methyl oleate, and other olefins, had prompted Farmer and other investigators to propose that hydroperoxides are the initial products of autoxidation. Because of the energy required to rupture an  $\alpha$ -methylene C-H bond, and for other reasons (48, 66), Farmer (28, 29), Bolland and Gee (16, 17), and Gunstone and Hilditch (34) more or less simultaneously concluded that the initial point of oxidative attack was at the double bond and *not* at the  $\alpha$ -methylene group. It was agreed that double bond attack must occur to only a minor extent, probably in sufficient amount to "trigger" the  $\alpha$ -methylene chain reaction which predominates by far. The evidence in the preceding section of the present paper on the non-hydroperoxide content of the peroxides isolated from autoxidized methyl oleate is in line with this conclusion.

Direct experimental evidence that hydroperoxides are not the sole peroxide species formed, even in the early stages of autoxidation of methyl oleate, was recently obtained by Saunders, Ricciuti, and Swern (54). These investigators followed the absorption of oxygen quantitatively over a wide range of oxygen uptake (15-300 millimoles per mole of methyl oleate) at 60-100° and then analyzed the resulting autoxidized methyl oleate for hydroperoxides (polarographically) and total peroxides (iodometrically). They showed that, of the total peroxides formed, only 90-95% could be accounted for as hydroperoxides.

Among the outstanding contributions to the mechanism of autoxidation of methyl oleate and other olefinic materials are the extensive studies on the kinetics of autoxidation described by Bateman, Bolland, and coworkers (2, 3, 3a, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 18, 19). There is no doubt that the low temperature liquid phase autoxidation of olefins occurs by a chain mechanism. Thus if inhibitors or initiators are added, spectacular decreases or increases in reaction rate, respectively, are observed; and if the reaction is accelerated photochemically, the quantum yield may exceed unity.

Comparison of the experimentally determined rate equations for the interaction of oxygen with olefins in the presence of benzoyl peroxide, ultra-violet radiation, or in the dark in the absence of added initiators shows an obvious parallelism in the way the rate of oxidation depends on  $[O_2]$  and  $[RH]$  (3a, 13). Kinetic analysis shows that photo- and non-photo-catalyzed oxidations proceed by the same basic mech-

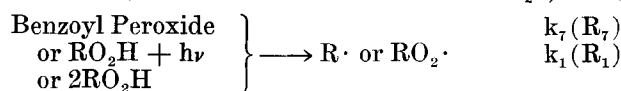
anisms. The three rate equations reduce to the common form:

$$\text{Rate} = R_1^{1/2} k [\text{RH}] \frac{[O_2]}{k' [\text{RH}] + [O_2]} \quad (\text{A})$$

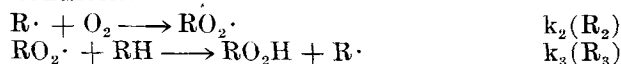
( $R_1$  is the rate of formation of chain carriers)

The kinetic characteristics embodied in this generalized relation can be accounted for in terms of a single chain-reaction mechanism as follows:

INITIATION (Production of radicals  $R\cdot$  or  $RO_2\cdot$ )  $R_1$



PROPAGATION



TERMINATION



The rate of oxidation is related to the velocity coefficient of the various elementary reactions ( $k_1$ - $k_7$ ) by

$$\frac{-d [O_2]}{dt} = R_1^{1/2} \frac{k_3}{\sqrt{k_6}} [\text{RH}] \frac{k_2 \sqrt{k_6} [O_2]}{k_3 \sqrt{k_4} [\text{RH}] + k_2 \sqrt{k_6} [O_2] + \sqrt{k_4 k_6 R_1}} \quad (\text{B})$$

The correspondence between the experimental (A) and the theoretical (B) relations is complete since the term  $\sqrt{k_4 k_6 R_1}$  becomes negligible at chain lengths as great as those encountered in these autoxidations.

The efficiencies with which the initiation process ( $R_1$ ) and the termination reaction ( $R_6$ ) occur are sensibly the same for a variety of non-conjugated unsaturated hydrocarbons. The resultant influence of the propagation and termination reactions involving the  $R$ -type chain carrier is negligible. The remaining chain-propagation step ( $R_3$ ) is sufficiently sensitive to the nature of  $RH$  to introduce considerable variations in oxidation-chain length;  $R_3$  must thus be regarded as the key reaction in controlling rates of autoxidation. Further details and discussion of these equations are given in Bolland's review on kinetics of olefin oxidation (13).

Chlorophyll also accelerates the autoxidation of oleic acid (10) in the light and dark (38), but the mechanism of the reaction is not known.

It is also worth noting that methyl oleate, free of linoleate, is remarkably resistant to autoxidation below 50° (35). Traces of linoleate rapidly propagate the autoxidation of oleate.

Recently Khan, Brown, and Deatherage (40), Max and Deatherage (47), and Khan (39) studied and compared the autoxidation of methyl oleate, methyl 9,10-dideuterioleate, and 8,8,11,11-tetradeutero-*cis*-octadecene. These investigators showed that deuterium compounds oxidize at a slower rate than do the corresponding hydrogen compounds. They concluded that initial autoxidative attack is at the double bond, and the main sustaining reaction is attack at the  $\alpha$ -position.

Khan (39a) has recently proposed a new mechanism, which is not in conformity with earlier ideas of Farmer and Hilditch, for the initial stages of autoxidation of methyl oleate (and other unsaturated esters). This involves interaction of oxygen and the olefin in activated states, followed by complex formation to yield transitory six membered rings. These on rearrangement, with a necessary shift of the double bond, yield the hydroperoxides which are the products isolated. Bateman (1a), on the other hand, has disputed Khan's interpretations and has noted that the formation of isomeric autoxidation products has nothing whatever to do with olefin-oxygen interaction but reflects the mesomerism of allylic free radicals or intramolecular rearrangement of peroxy radicals.

*Secondary Products of Autoxidation.* Noteworthy contributions have recently been made to the study and separation of secondary products of autoxidation of oleic and elaidic acids and their esters by Ellis (26, 27), Skellon (32a, 57, 58, 59, 60, 61, 62), King (40), and investigators from this laboratory (21, 22, 41, 43, 44). The main products, which result from transformation or decomposition of initially formed hydroperoxides, are 9,10-epoxy- and 9,10-dihydroxystearic acids,  $\alpha,\beta$ -unsaturated keto acids, and cleavage products.

It was recently shown that in the uncatalyzed autoxidation of methyl oleate substantially all of it undergoes single attack by oxygen or peroxides before any significant quantity of multiple attack in the chain occurs (21). A typical composition, after the peak in peroxide content has been passed, is about 30-35% peroxide, 25-30% hydroxy compounds, 20-25% oxirane compounds, 15-20%  $\alpha,\beta$ -unsaturated carbonyl compounds and some residual methyl oleate, cleavage products, polymers, and multiply attacked methyl oleate. Hydrogenation of such mixtures with Raney nickel and palladium as catalysts yields monohydroxystearic acids in high yield (22).

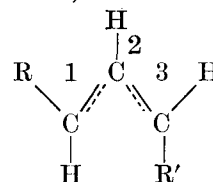
$\alpha,\beta$ -unsaturated carbonyl compounds have been isolated by Ellis (26, 27) from autoxidized oleic and elaidic acids. These products would appear to be obtained directly from the corresponding  $\alpha$ -methylene hydroperoxides simply by the loss of a molecule of water. 12-Ketoelaidic and 12-ketooleic acids, isomers of the  $\alpha,\beta$ -unsaturated carbonyls obtained in autoxidation, have been prepared synthetically by controlled oxidation of ricinelaidic and ricinoleic acids (27). 12-Ketoelaidic acid is relatively stable toward autoxidation whereas 12-ketooleic acid absorbs oxygen even at 0°. This relative autoxidizability is of particular significance because we have shown that most, if not all, of the hydroperoxides formed from methyl oleate have the *trans* configuration. The  $\alpha,\beta$ -unsaturated carbonyl compounds derivable from these hydroperoxides should also be *trans* since dehydration does not involve the double bond. Although the  $\alpha,\beta$ -unsaturated carbonyls formed during autoxidation are not identical with 12-ketoelaidic acid they are closely related, and it might be assumed that they too would be resistant to further autoxidative attack in the absence of catalysts. The fact that single attack on the methyl oleate chain predominates supports this conclusion; otherwise a significant amount of multiple attack would occur before all the methyl oleate had been autoxidized.

It is known that oxirane compounds are also resistant to further autoxidative attack at moderate temperatures, and it would appear that the unsatu-

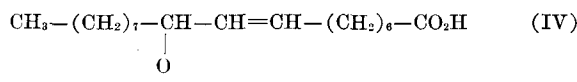
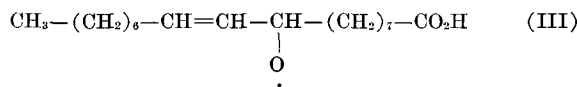
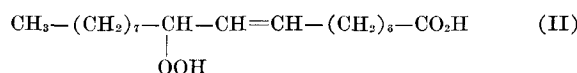
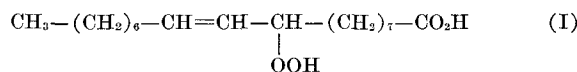
rated hydroxy compounds must be too. Although this latter point has not been resolved experimentally, it is probable that the hydroxy compounds, as well as some of the oxiranes, are converted to esters, thereby enhancing their stability.

King (40a) has recently published a detailed analytical study of the autoxidation of elaidic acid at 47° and 78° with and without a cobalt salt catalyst. The formation of ketol derivatives has been confirmed, and formic acid has been identified among the volatile products of autoxidation. Methods were also reported for estimating ketol and other carbonyl compounds.

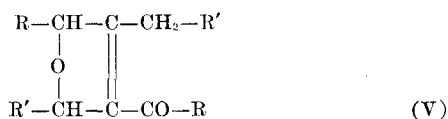
It was shown by Ellis (25) that both oleic and elaidic acids on autoxidation give *trans*-9,10-epoxystearic acid in about 20% yield. The fact that both a *cis* and a *trans* compound yield the same, rather than different products by the identical oxidation method is indeed surprising and remained unexplained for many years. With the development of infrared spectrophotometric methods for determining *trans* compounds in autoxidized and other materials (42, 55, 64), it was shown that the majority of radicals in the autoxidation of oleic (and elaidic) acid take the configuration shown below,



and add oxygen at carbon atom 3 (42). The resulting hydroperoxides, 9-hydroperoxido-10-*trans*-octadecenoic acid and 10-hydroperoxido-8-*trans*-octadecenoic acid (I and II), on homolytic cleavage yield the radicals HO· and RO· (III and IV). Both III and IV, by shift of one  $\pi$ -electron of the double bond to couple with the odd electron on oxygen, would form the oxirane ring in the 9,10-position. Reacquisition of a hydrogen atom then yields *trans*-9,10-epoxystearic acid.



In the uncatalyzed autoxidation of methyl oleate, polymer formation does not occur until advanced stages (21). When metal catalysts are present however, polymers form even in the early stages. The structure of the polymers formed from autoxidizing methyl oleate is not known. Evidence has been published suggesting that they are largely oxygen-linked (17, 50, 65) as distinguished from methyl linoleate polymers in which carbon-carbon linkages are known to be present certainly in the dimers (50, 72). Ellis (26) has proposed that the dimers from autoxidized oleic acid are substituted dihydrofurans (V) which are formed from the  $\alpha,\beta$ -unsaturated carbonyls.



Swift, Dollear, Brown, and O'Connor (68) have shown that one of the decomposition reactions of methyl oleate hydroperoxides is cleavage to  $\alpha,\beta$ -unsaturated carbonyls, one of which is 2-undecenal. Swift and Dollear (67) have reported that oleic acid can be intermolecularly oxidized at 90° by methyl oleate hydroperoxides to form *cis*-9,10-epoxystearic acid, m.p. 59°, and low melting (but *not* high-melting) 9,10-dihydroxystearic acid, m.p. 95°, in small quantity.

Recently Ahlers and McTaggart (1) have devised infrared spectroscopic methods for the quantitative determination of secondary products of autoxidation, such as hydroxy and carbonyl compounds. The method requires only about 20 milligrams of sample (which can be recovered after examination), and the accuracy of each determination is similar to that of the corresponding conventional chemical method.

### Summary

Some significant developments since 1947 in the autoxidation of methyl oleate and other monounsaturated fatty materials have been reviewed and critically evaluated. Subjects discussed are preparation and characterization of hydroperoxides, and mechanism, kinetics, and secondary products of autoxidation. Major developments in the field have resulted largely from the use of newer instruments (polarograph, infrared spectrophotometer) and separation techniques (urea complexes, molecular distillation, countercurrent distribution).

Direct experimental evidence is now available which demonstrates that a) hydroperoxides are the predominating, but not the exclusive, primary products of autoxidation; b) the hydroperoxides obtained from methyl oleate are mostly, if not entirely, *trans*; c) substantially all the methyl oleate undergoes single attack in the chain before any significant amount of multiple attack occurs, and d)  $\alpha,\beta$ -unsaturated carbonyl compounds are among the most important secondary products of autoxidation.

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